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A STUDY OF SELECTIVE ADSORPTION BY LIGHT SCATTERING

A THESIS

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BY LIGHT SCATTERING

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NOMENCLATURE

a	empirecal constant
A	empirical constant
A_2	second virial coefficient
B	empirical constant
c	concentration
d	deflection of refractometer beam, density
G	galvanometer reading, Gibbs free energy
I_o	intensity of incident light
i_θ	intensity of scattered light
K	optical constant in light-scattering equation
K'	empirical constant
k	empirical constant
M	molecular weight
$\bar{M}_n$	number-average molecular weight
$\bar{M}_v$	viscosity-average molecular weight
$\bar{M}_w$	weight-average molecular weight
$\bar{M}_w^*$	apparent weight-average molecular weight
N	Avogadro's number
n	refractive index
$P(\theta)$	intramolecular scattering function
R_θ	reduced scattering intensity
R	gas constant, specific refraction

r	distance from the center of the scattering cell to the photocell
R_G	radius of gyration
T	absolute temperature, transmittance
t	flow time
V	molar volume
v	volume fraction
w	weight fraction
α	selective adsorption constant
η	viscosity
$[\eta]$	intrinsic viscosity
η_{sp}	specific viscosity
λ	wavelength of light
ρ	density, depolarization
θ	light scattering angle
β	empirical constant
χ_{ij}	binary interaction parameter
χ_{ijk}	ternary interaction parameter
μ	chemical potential

SUMMARY

A study of the selective adsorption of a liquid from a mixed solvent system by polymer molecules was carried out by light scattering method of Ewart, Roe, Debye and McCartney. The basis of this method is that the apparent weight average molecular weight of a polymer is a function of both the extent of selective adsorption and the difference in refractive indices of the two liquids which constitute the binary solvent mixture.

The systems studied were the following: polyisobutylene in cyclohexane and acetone, polyisobutylene in cyclohexane and benzene, and polymethylmethacrylate in acetone and cyclohexane. The polymethylmethacrylate samples had different degrees of stereoregularity.

The light scattering data were treated by Zimm method, eliminating the dissymmetry effect by extrapolating to both zero polymer concentration and zero scattering angle.

For the polyisobutylene-cyclohexane-acetone system, cyclohexane is preferentially adsorbed by the polymer molecules. The interaction parameter χ_{23} between polyisobutylene segments and acetone molecules is estimated to be 2.0 ± 0.1.

The measurements on polyisobutylene in the mixed solvent cyclohexane-benzene were less successful because the refractive index of benzene (1.5149) is too close to that of polyisobutylene (1.5282). Consequently the excess scattering is too small for the measurement

to have sufficient precision to be reliable. Therefore, only one successful measurement was made, at a benzene concentration of 20 per cent by volume. The result of this measurement shows that the poorer solvent, benzene, is selectively adsorbed. This result is in agreement with theoretical predictions based upon the Flory-Huggins theory of polymer solutions.

The results of the measurements on the stereoisomers of polymethylmethacrylate show that the extent of selective adsorption is not affected by the local order of the side chain in this polymer.

For each system studied, Read's theoretical treatment of selective adsorption was used to analyze the experimental results. Although his equation does not fit the experimental results well, it is nevertheless useful in predicting which of the solvent constituents will be selectively adsorbed and in estimating the extent of the selective adsorption, provided that values of the relevant interaction parameters of the system are known.

CHAPTER 1

INTRODUCTION

"Selective adsorption" is a term which is used in polymer solution theory. When a polymer substance is dissolved in a mixed solvent consisting of liquids A and B to form a uniform dilute solution, selective adsorption can be said to occur if the composition of the mixed solvent in the vicinity of the polymer molecules is different from that of the original solvent mixture.

There are several ways of studying selective adsorption experimentally, e.g., ultracentrifugation (1), diffusion (2) and light scattering measurements. Since a light scattering photometer was available, the present study was carried out by a light scattering method. The basis of this method is that, in general, the addition of a second liquid to a polymer-solvent mixture causes a change in the amount of light scattered as a result of the selective adsorption of one or other of the solvent components by polymer molecules. This selective adsorption is a measure of the change in composition of the solvent mixture in the vicinity of the polymer segments.

Light scattering in mixed solvent systems is a valuable method for evaluating parameters characteristic of the interactions of polymer segments with solvent molecules. It is of particular interest if one of the solvent components is a non-solvent, for there is no way to measure the interaction parameter between a polymer and a non-solvent directly.

Theoretical and Experimental Backgrounds

Light scattering is a powerful technique for obtaining information on polymer solutions. It was first applied to the study of polymer solutions by Putzeys (3). In 1944 Debye (4) showed how the experimental data on the light scattering of the polymer solution could be treated to obtain such valuable information as the weight average molecular weight $\bar{M}_w$ and the molecular dimensions of the polymer molecules in the solution. But the study of selective adsorption by light scattering was not begun until 1946, when Ewart, Roe, Debye and McCartney (5) extended the theory of light scattering to the treatment of three component systems consisting of a polymer and two solvent constituents. Their theory predicts that if the data are treated in the usual manner that the right value of weight average molecular weight will be obtained only if the refractive index of the solvent mixture is independent of its composition. If the solvent components used have sufficient difference in their refractive indices, the light scattering measurements will show the extent of selective adsorption of solvent by the polymer segments. This theory was then tested by their experiments with polystyrene, which showed that good solvents were preferentially adsorbed.

Another theory of light scattering for multicomponent systems, due to Kirkwood and Goldberg (6) and independently to Stockmayer (7), is an extension of the Einstein fluctuation theory to systems which contain a number of components. They developed the expression for the fluctuation of refractive index in multi-component systems, which is related to the excess scattering. The average value of squared

fluctuation of refractive index depends on concentration dependence of the chemical potential of each species with respect to its own concentration and on the concentration dependence of the chemical potential of each species with respect to the other species.

The outline of the theory leading to the selective adsorption expression is given in the following. In order to understand the scattering phenomena, we start by considering the scattering of light by a gas. Since the gas particles are randomly located, each particle acts as an independent source of scattered radiation. On the other hand, the particles of a crystal are ordered in space relative to one another. Consequently there is a destructive interference between light scattered from the individual particles. Therefore perfect crystals scatter very little light. Liquids are intermediate between gases and crystals. The thermal motion of the molecules causes density fluctuations which in turn are associated with refractive index fluctuations. It is this inhomogeneous distribution of refractive index that causes the scattering of light. In case of solutions, there is an additional contribution due to the fluctuations in concentration of the solute particles. When unpolarized light is forced to fall on a dilute polymer solution, the resulting intensity of light scattered is the sum of the contributions of each independent particle. The light scattered at an angle θ from the direction of the incident light is related to the molecular weight by the equation (8)

$$\frac{i_\theta}{I_o} = \frac{\pi^2(1 + \cos^2\theta)\left(\frac{n^2 - n_m^2}{c}\right)^2 Mc}{2N\lambda^4 r^2} \qquad (1)$$

where i_θ = intensity of the scattered light at angle θ;

I_o = intensity of the incident light;

c = concentration of solution (g./ml. solution);

N = Avogadro's number;

λ = wavelength of light;

r = distance from the center of the scattering cell to the photocell;

M = molecular weight of the solute;

n = refractive index of the solution

n_m = refractive index of the solvent medium surrounding a solute molecule.

This equation is true only for ideal solutions. However, polymer solutions frequently exhibit very large deviations from ideality due to large entropies of mixing. For non-ideal solutions Equation (1) must be replaced by

$$\frac{i_\theta}{I_o} = \frac{\pi^2(1 + \cos^2\theta)\left(\frac{n^2 - n_m^2}{c}\right)^2 c}{2N\lambda^4 r^2(1/M + 2A_2c + 3A_3c^2 + \ldots)} \qquad (2)$$

where A_2 and A_3 are virial coefficients. Equation (2) can be written

in the following form

$$\frac{Kc}{R_\theta} = 1/M + 2\,A_2 c + 3\,A_3 c^2 + \ldots \tag{3}$$

where K (optical constant) $= \dfrac{\pi^2 \left(\dfrac{n^2 - n_m^2}{c}\right)^2}{2\,N\lambda^4}$ (4)

$$R \text{ (Rayleigh ratio)} = r^2 i_\theta / I_o (1 + \cos^2\theta) \tag{5}$$

Polymer samples always consist of many different species of different molecular weight. Considering species i with molecular weight M_i and number of molecules N_i, we can write:

$$c_i = N_i M_i / V \quad \text{and} \quad c = \sum_i c_i = \frac{1}{V} \sum_i N_i M_i \tag{6}$$

where V is the volume of the solution. In very dilute solutions, where each scattering particle is independent of one another, the total scattering is the sum over all species. Therefore

$$(R_\theta)_{c=0} = \sum_i R_i = K \sum_i c_i M_i \tag{7}$$

Combining Equations (6) and (7), we get

$$(R_\theta)_{c=0} = K \frac{c \sum_i c_i M_i}{\sum_i c_i} = Kc \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \tag{8}$$

The weight average molecular weight $\bar{M}_w$ is defined as $\sum_i N_i M_i^2 / \sum_i N_i M_i$. Thus Equation (8) becomes $(R_\theta)_{c=0} = Kc\bar{M}_w$. It is clear the weight average molecular weight is the quantity obtained from light scattering, if the solute is a polydisperse sample. For a very dilute solution, we can write

$$\left(\frac{Kc}{R_\theta}\right)_{c=0} = 1/\bar{M}_w \tag{9}$$

Also $n + n_o \tilde{=} 2n_o$, $n - n_o \tilde{=} (dn/dc)\, c$

so $(n^2 - n_m^2) = (n^2 - n_o^2) = 2n_o(dn/dc)\, c$

where n_o is the refractive index of solvent medium, which is equal to n_m for the case of a pure solvent. The optical constant K becomes

$$K = 2\pi^2 n_o^2 (dn/dc)^2 / N\lambda^4 \tag{10}$$

For the case of a polymer in a mixed solvent, n_o is no longer equal to n_m if there is a preference for one of the two solvents to be found in the vicinity of the polymer segments. Denoting v_1 as the volume fraction of component "1" of the solvent mixture, we can write:

$$(n^2 - n_m^2) = (n^2 - n_o^2) + (n_o^2 - n_m^2)$$

$$= (2n_o)\,(dn/dc)c + n_o^2 - (n_o^2 + (dn_o/dv_1)^2 \Delta v_1)$$

thus $$\frac{n^2 - n_m^2}{c} = 2n_o(dn/dc) - 2n_o(dn_o/dv_1)(dv_1/dc)$$

or $$\left(\frac{n^2 - n_m^2}{c}\right) = 4n_o^2(dn/dc + \alpha\, dn_o/dv_1)^2$$

where $\alpha = - dv_1/dc$ (11)

The quantity α is called the selective adsorption coefficient because it provides a measure of the tendency of polymer molecules to remove solvent "1" from the surrounding medium. The optical constant K in Equation (4) is

$$K^* = \frac{2\pi^2 n_o^2}{\lambda^4 N}(dn/dc + \alpha\, dn_o/dv_1)^2 \qquad (12)$$

$$= K[1 + \alpha(dn_o/dv_1)/(dn/dc)]^2$$

and Equation (9) is replaced by

$$\frac{K^* c}{R_\theta} = 1/\bar{M}_w \qquad (13)$$

If instead, we use the normal optical constant K instead of K^*, we can write

$$\frac{Kc}{R_\theta} = 1/\bar{M}_w^* \qquad (14)$$

where $\bar{M}_w^*$ is an "apparent" weight average molecular weight. Comparing Equation (13) and Equation (14), we obtain

$$K^*\bar{M}_w = K\,\bar{M}_w^*$$

Substituting K^* from Equation (12) into above equation, we can write

$$[1 + \alpha(dn_o/dv_1)/(dn/dc)]^2\bar{M}_w = \bar{M}_w^*$$

or

$$\alpha = \left[\left(\frac{\bar{M}_w^*}{\bar{M}_w}\right)^{\frac{1}{2}} - 1\right]\left[\frac{(dn/dc)}{(dn_o/dv_1)}\right] \qquad (15)$$

Thus we see that $\bar{M}_w^*$ will vary with the composition of the mixed solvent if there is any selective adsorption ($\alpha \neq 0$) except in the special case where the two solvent constituents have the same refractive index ($dn/dv_1 = 0$).

The theoretical approach outlined so far does not apply if the dimensions of the solute particles are comparable with the wavelength of the incident light. The reason for this is that the paths of the scattered light from different parts of the polymer molecule are different except at zero angle where there is no destructive interference. Thus the theoretical approach outlined above can be used for solutions of large particles only if the light scattering data are obtained at several angles and extrapolated to zero angle. It is customary to express this intramolecular effect by the intramolecular scattering function $P(\theta)$, which is the ratio of observed intensity to the scattered intensity at an angle θ without interference, normalized to unity

at zero scattering angle. Equation (3) is then modified to read

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w P(\theta)} + 2A_2 c + 3A_3 c^2 + \ldots \qquad (16)$$

Equation (3) shows that a plot of (Kc/R_0) vs. c can be used to calculate both the weight average molecular weight $\bar{M}_w$ and the second virial coefficient A_2. Upon the addition of a precipitant to a dilute polymer solution, the solvent medium becomes poorer. Hence the initial slope of this plot decreases because of the contraction of the swollen molecules. Also, the intercept of the infinite dilute extrapolation will either increase or decrease as selective adsorption occurs, cf. Equation (15). If the solvent component adsorbed has the higher value of refractive index and $\alpha > 0$, the intercept should decrease. The contrary would be true if the refractive indices were in the reverse order. Thus, the change in the intercept is an indication of the selective adsorption of a constituent of the solvent by the polymer segments.

Yoshino and Tanzawa (2) recommended an easy way to study the selective adsorption, which they claimed is superior to the light scattering method. They measured the diffusion through the interface between the solution phase and pure mixed solvent phase. At equilibrium the composition of the solvent mixture is less than that of the initial solvent mixture used for making the polymer solution by the amount preferentially adsorbed. Two systems, toluene-isobutanol-polystyrene and benzene-cyclohexane-polystyrene, were studied by light scattering

measurement and diffusion measurement. The latter was proved to be more accurate than the former.

Blaker and Badger (9) studied the interaction of nitrocellulose with several solvents and non-solvents, using the light scattering method. The additives, second solvents, were either a poorer solvent or a non-solvent. They found that the additive was selectively adsorbed in each case. This surprising result was rationalized by assuming that nitrocellulose molecules could be visualized as a ribbons with polar groups along the edges, but with non-polar faces.

Brouckere and Anspach (10) measured the light scattering of polystyrene in mixtures of toluene with normal hexane, normal heptane, ether, dioxane, acetone, butanone, cyclohexane and secondary butanol. They found that the good solvent toluene was selectively adsorbed in every case except that of cyclohexane.

An early theoretical paper by Kawai (11) developed an expression for the magnitude of selective adsorption from the knowledge of certain interaction parameters characterizing the polymer-mixed solvent system. Hence the magnitude of selective adsorption in any system can be estimated once the values of these interaction parameters are known. His theory should be applicable to the case where the selective adsorption is studied by light scattering, but has not been applied in this manner to date.

Applying the Flory-Huggins lattice model theory of polymer solutions (12,13) to the problem of selective adsorption on the system benzene-cyclohexane-polystyrene, Read (14) derived a theoretical description of the adsorption constant α as function of the solvent

composition. According to the fluctuation theories of Stockmayer (7) and of Kirkwood and Goldberg (6), the adsorption constant is proportional to the quantity

$$\frac{(\partial\mu_2/\partial m_3)_{T,P,m_2\to 0}}{(\partial\mu_2/\partial m_2)_{T,P,m_3\to 0}},$$

i.e., $$\alpha = \frac{V_2}{V_3}\bar{v}_3\, v_1\left(\frac{\partial\mu_2}{\partial m_3}\right)_{T,P,m_2\to 0}/(\partial\mu_2/\partial m_2)_{T,P,m_3\to 0},$$

where μ_2 is the chemical potential of solvent 2, and m_2 and m_3 are concentrations in moles per unit mass of component 1. The quantities $(\partial\mu_2/\partial m_3)_{T,P,m_2\to 0}$ and $(\partial\mu_2/\partial m_2)_{T,P,m_3\to 0}$ are obtained from the Gibbs free-energy change. The Gibbs free-energy change accompanying the mixing of the three components can be written as

$$\Delta G_M/RT = m_1 \ln v_1 + m_2 \ln v_2 + m_3 \ln v_3 + \chi_{12} m_1 v_2 + \chi_{13} m_1 v_3 + \chi_{23} m_2 v_3 .$$

Hence $$\frac{\mu_2 - \mu_2^\circ}{RT} = \frac{1}{RT}\left(\frac{\partial \Delta G_M}{2m_2}\right)_{T,P,m_3}$$

$$= \ln v_2 + (1 - v_2) - \ell^{-1} v_1 + (\chi_{12}\ell^{-1} v_1 + \chi_{23} v_3)(v_1 + v_3) - \chi_{13}\ell^{-1} v_1 v_2 .$$

Differentiating μ_2 with respect to m_2 and m_3 and eliminating terms in v_3, we obtain

$$\alpha = \bar{v}_3 v_1 v_2 \frac{[\chi_{12}\ell^{-1}(v_2 - v_1) + \chi_{23} - \ell^{-1}\chi_{13} + (\ell^{-1} - 1)]}{v_1 + \ell^{-1}v_2 - 2\chi_{12}\ell^{-1}v_1 v_2} \qquad (17)$$

where v_1, v_2 = volume fraction of liquids in the binary phase;

$\ell = V_1/V_2$;

V_1, V_2 = molar volume of liquid (1) and liquid (2), respectively;

$\bar{v}_3$ = specific volume of polymer;

$\chi_{12}, \chi_{23}, \chi_{13}$ = interaction parameters.

The parameter χ_{ij} is related to the free energy change in the formation of molecular contact between species i and j. A large value of χ_{ij} indicates that the molecular contact is unfavorable, e.g., a large value of χ_{13} means that the solvent power for the polymer is poor. The magnitude of selective adsorption can also be calculated by his treatment, if the binary interaction parameters χ_{12}, χ_{23} and χ_{13} are known. Also he suggested that a ternary interaction parameter χ_{123} is required in order to fit his experimental results better. χ_{123} is a three-body interaction parameter, which is related to the free energy change accompanying the formation of the triple molecular contact of species 1, 2, and 3.

Cowie and Bywater (15) studied the light scattering of polystyrene in mixtures of benzene-heptane, benzene-isopropanol and dioxane-heptane. The good solvent was preferentially adsorbed in each case. Their data were also better fit by Read's equation if a ternary interaction parameter χ_{123} was used.

Scope and Purpose of the Study

In this work, the light scattering behavior of polyisobutylene (PIB) in the mixed solvent systems cyclohexane-acetone and cyclohexane-benzene was studied. The experimental data were used to test Read's theoretical description of selective adsorption. The interaction parameter of PIB with acetone χ_{23} was so chosen that the adsorption constant α gave the best agreement with the theoretical prediction. A direct measurement of this value can not be made.

Also, polymethylmethacrylate (PMMA) samples having different degrees of stereoregularity have been studied in the mixed solvent system acetone-cyclohexane. The purpose of this investigation was to study the influence on the selective adsorption of the local order along the chain by comparing the differences in the adsorption constant α.

For the case where the polymer is either PIB or syndiotactic PMMA the light scattering data were plotted by Zimm method (16) eliminating the dissymmetry effect by extrapolating to both zero polymer concentration and zero angle. A plot of $(Kc/R)_{\theta=0}$ versus c was constructed for atactic PMMA-acetone-cyclohexane system. The selective adsorption constant was calculated from the apparent weight average molecular weight by Equation (15).

CHAPTER II

SELECTIVE ADSORPTION MEASUREMENT

A Brice-Phoenix light scattering photometer (17) was used for this study. Unpolarized incident radiation of both 4358 Å and 5461 Å was used when the polymer was PIB. A single wavelength of 4358 Å was used for the case where the polymer was PMMA. Measurements was made at temperatures of 35° C and 25° C when the mixed solvent systems were cyclohexane-acetone and cyclohexane-benzene, respectively. The system polymethylmethacrylate-acetone-cyclohexane was studied at 25° C.

The solutions were made up by weight and were evaporated to dryness after measurement. A microbalance was used to weigh (to ± 0.1 mg.) the amount of polymer remaining in a volume of solution measured at room temperature. The exact concentration was calculated and corrected to the experimental temperature from the known densities of the mixed solvent at the two different temperatures. For this purpose the additivity of volumes was assumed.

To effect purification from dust, each solution was carefully filtered through an ultrafine glass-sintered filter under nitrogen pressure of 14 psi (3 psi in the case of polymethylmethacrylate solutions) into a previously cleaned cell. It was found, however, that this filtration procedure was not satisfactory when acetone was a main constituent of the solvent mixture. It was found that by holding a Tesla coil near the filter during the filtration that satisfactory filtration

was effected for this system.

Polymer and Solvent

Polyisobutylene

The polyisobutylene sample used was a commercial Vistanex, designated L-80. It has a ratio of weight average molecular weight to number average molecular weight of about 3 (18). It was fractionated in the following manner (18). Small pieces were dissolved in cyclohexane to yield a solution of about 1 per cent polymer. It was precipitated by adding the solution to acetone in a Waring Blender, with agitation. The polymer phase was separated and then washed with a small amount of cyclohexane, by which it was hoped to re-dissolve the low molecular weight tail. Then the polymer was dissolved in benzene, followed by the addition of a small amount of methanol to remove the high molecular weight tail. The polymer obtained was then dried to constant weight under vacuum at about 60° C. The sample resulting from this treatment was designated L-80F.

Polymethylmethacrylate

The polymethylmethacrylate samples and characterization data were provided by Dr. T. G. Fox of the Mellon Institute. Sample No. BDK-III is an ideally atactic polymethylmethacrylate with P[S] = 0.5, P[I] = 0.5, and $\bar{M}_{vis} \sim 100{,}000$. It has a broad molecular weight distribution. Sample No. NC-PMMA No. 5 is a 60° free radical, conventional PMMA with P[S] = 0.765, P[I] = 0.235, and $\bar{M}_{vis} \sim 700{,}000$, $\bar{M}_w/\bar{M}_n = 2$. This sample is essentially syndiotactic. The definitions of the quantities P[S] and P[I] are those of Fox (19). P[S] and P[I]

are probabilities that placements selected at random are syndiotactic and isotatic placements, respectively.

Cyclohexane

Reagent quality cyclohexane (Matheson Coleman and Bell quality control code 2825 CX2290) was purified by drying overnight with calcium chloride, followed by distillation. The apparatus used in this work is shown in Figure 1. After refluxing for one hour, the distillate was collected in a 2-l. flask. After collecting 50 ml. of distillate, the temperature increased from 81° C to 81.4°C, which is the boiling point of cyclohexane. The final product was collected at 81.4 °C in a 5-l. flask. The reflux ratio was set at about 7 to 1 during this process.

The distilled cyclohexane was then passed through a 0.5 m. (D_{in} = 1") column packed with silica gel to adsorb any aromatic compounds. Finally, the purified cyclohexane was stored over sodium wire.

Acetone

The purification of acetone was done in two steps: first the impurities were oxidized by use of $KMnO_4$, and second, the product was dehydrated chemically with P_2O_5.

Reagent grade acetone (J. T. Baker) was refluxed over $KMnO_4$ for one night to oxide such impurities as alcohols. It was then distilled into a flask containing calcium chloride. Since calcium chloride is only a moderately strong dehydrating agent, this was followed by a distillation from P_2O_5, with the vapor passing through a tube containing additional P_2O_5. The anhydrous acetone was kept in the refrigerator.

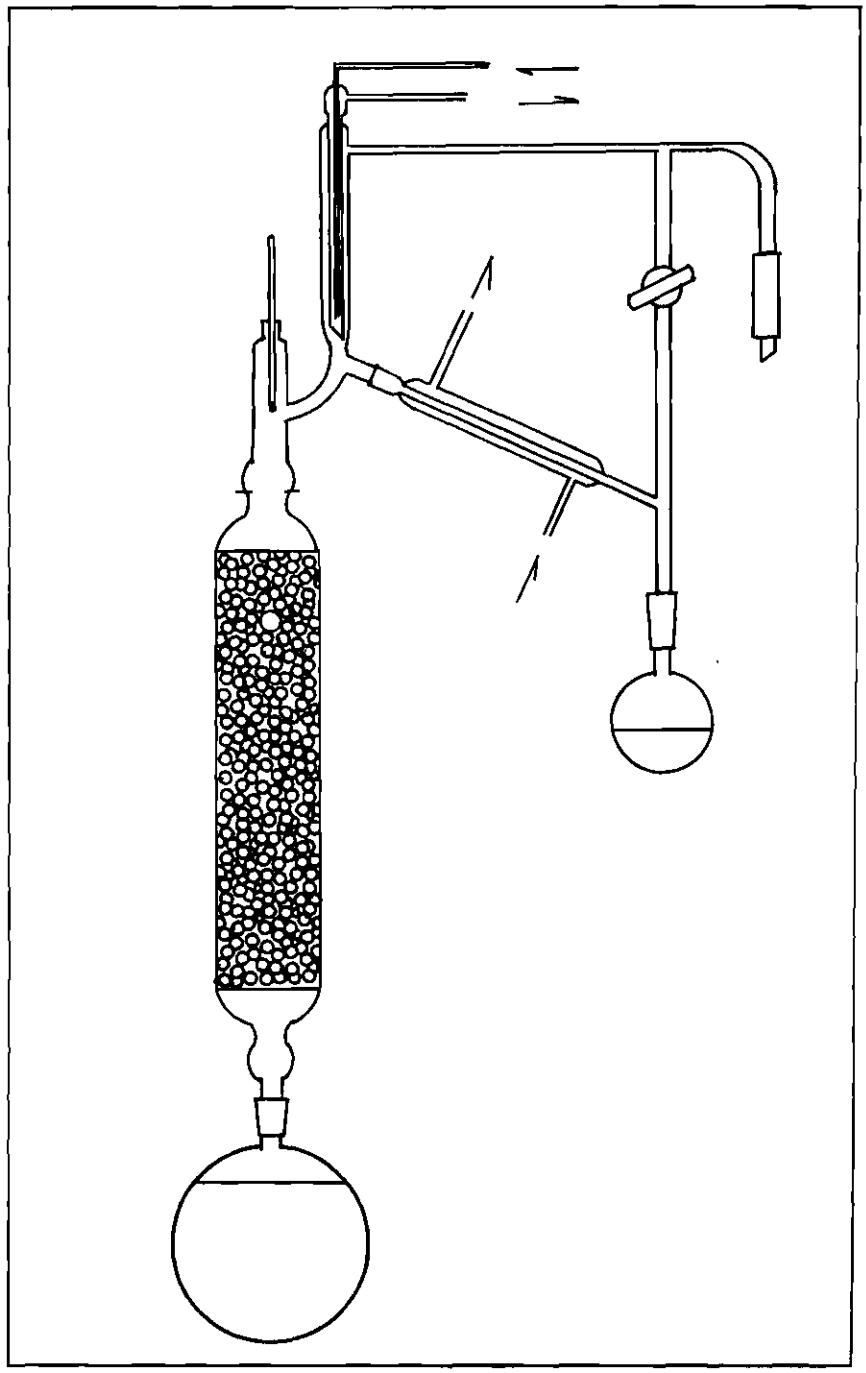


Figure 1. Fractional Distillation Apparatus

Benzene

Reagent grade benzene (J. T. Baker) was purified by shaking with Drierite for one day, followed by distillation.

All the solvents were redistilled shortly before using.

Viscometry

Mark (20) and Houwink (21) showed that the molecular weight of a polymer is empirically related to the intrinsic viscosity, $[\eta]$ by the simple equation

$$[\eta] = K' M^a \tag{18}$$

where both K' and a are constants whose values depend on the nature of polymer, solvent and the temperature. They can be determined by measuring the intrinsic viscosities of several fractions of polymer, the molecular weights of which are known from light scattering or osmometry. If log $[\eta]$ is plotted against log M, a straight line will be obtained with slope a and intercept log K'. The values of K' and a for our system have been found to be 2.6×10^{-4} and 0.70, respectively (22).

The intrinsic viscosity, $[\eta]$, is defined by the relation

$$[\eta] = \lim_{c \to 0} (1/c)\,(\eta - \eta_o)/\eta_o = \lim_{c \to 0}(\eta_{sp})/c \tag{19}$$

where c = concentration of polymer in solution;

η = viscosity of polymer solution;

η_o = viscosity of the pure solvent;

η_{sp} = specific viscosity.

If a solution of polydisperse polymer is extremely dilute, the individual particles can be assumed to contribute to the viscosity independently of one another. Thus, the value η_{sp} is the sum of the contribution due to every species. For the species i, $(\eta_{sp})_i = K' M_i^a c_i$ according to Equation (18). Therefore

$$\eta_{sp} = \sum_i (\eta_{sp})_i = \sum_i K' M_i^a = K' \sum_i M_i^a c_i \tag{20}$$

From the definition of intrinsic viscosity, we obtain

$$[\eta] = \eta_{sp}/c = K' \sum_i M_i^a (c_i/c) = K' \sum_i w_i M_i^a$$

where w_i is the weight fraction of species i. If we define the viscosity average molecular weight $\bar{M}_v$ as

$$\bar{M}_v = \left(\sum_i w_i M_i^a\right)^{\frac{1}{a}} \tag{21}$$

Then Equation (20) can be written as follows:

$$[\eta] = K' \bar{M}_v^a \tag{22}$$

Thus from the measurement of the intrinsic viscosity, $[\eta]$, the viscosity average molecular weight $\bar{M}_v$ is obtained if the polymer is a

polydisperse sample.

The procedure for measuring the intrinsic viscosity is to measure the viscosities of several dilute solutions of different polymer concentration. The viscosity is related to the concentration in solution sufficiently dilute by the Huggins Equation (23)

$$\left(\frac{\eta - \eta_o}{\eta_o}\right)/c = \eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (23)$$

where k is an empirical constant. A plot of η_{sp}/c versus c gives a straight line with an intercept $[\eta]$ and slope $k[\eta]^2$. Another relationship, similar to the Huggins equation, is

$$\frac{1}{c} \ln (1 + \eta_{sp}) = [\eta] - \beta[\eta]^2 c \qquad (24)$$

A plot of $\frac{1}{c} \ln(1 + \eta_{sp})$ against c yields a straight line with intercept $[\eta]$ and slope $-\beta[\eta]^2$. It provides a check to plot both η_{sp}/c and $\frac{1}{c} \ln(1 + \eta_{sp})$ versus c on the same graph, since both straight lines should have common intercept. Furthermore, by expanding the natural log of Equation (24) and neglecting the terms higher than the second powers, we obtain

$$\frac{1}{c} \ln(1 + \eta_{sp}) = \frac{\eta_{sp}}{c} - \left(\frac{\eta_{sp}}{c}\right)^2 \frac{c}{2} \qquad (25)$$

Substituting Equation (23) into Equation (25) and ignoring the terms higher than square, we rewrite Equation (25) as

$$\frac{1}{c} \ln(1 + \eta_{sp}) = [\eta] + (k - \frac{1}{2}) [\eta]^2 c$$

Comparing the above equation with Equation (23), we find $k + \beta = 0.5$, which provides another check.

Intrinsic Viscosity Measurement

The viscometer used was a Ubbelohde dilution viscometer and is shown in Figure 2. It was immersed in a thermostat, the temperature of which was regulated to ±0.02 °C. A Meyland stopwatch, type 200A, was used to measure the flow times of solvent and solution to ±0.05 sec.

Calibration of Viscometer. The Poiseuille equation, corrected for kinetic energy and end-effects, can be written in the following form

$$\eta/\rho t = A - B/t^2 \qquad (26)$$

where η = viscosity of the liquid;

ρ = density of the liquid at a given temperature;

t = flow time;

A, B = constants to be determined by calibration.

Water was used to calibrate the viscometer because the densities and viscosities of water at different temperature are known accurately (24). Flow times of water at several different temperatures were measured in the way described in "Viscosity Measurement" section. If $(\eta/\rho t)$ versus $1/t^2$ is plotted, a straight line is obtained with B as

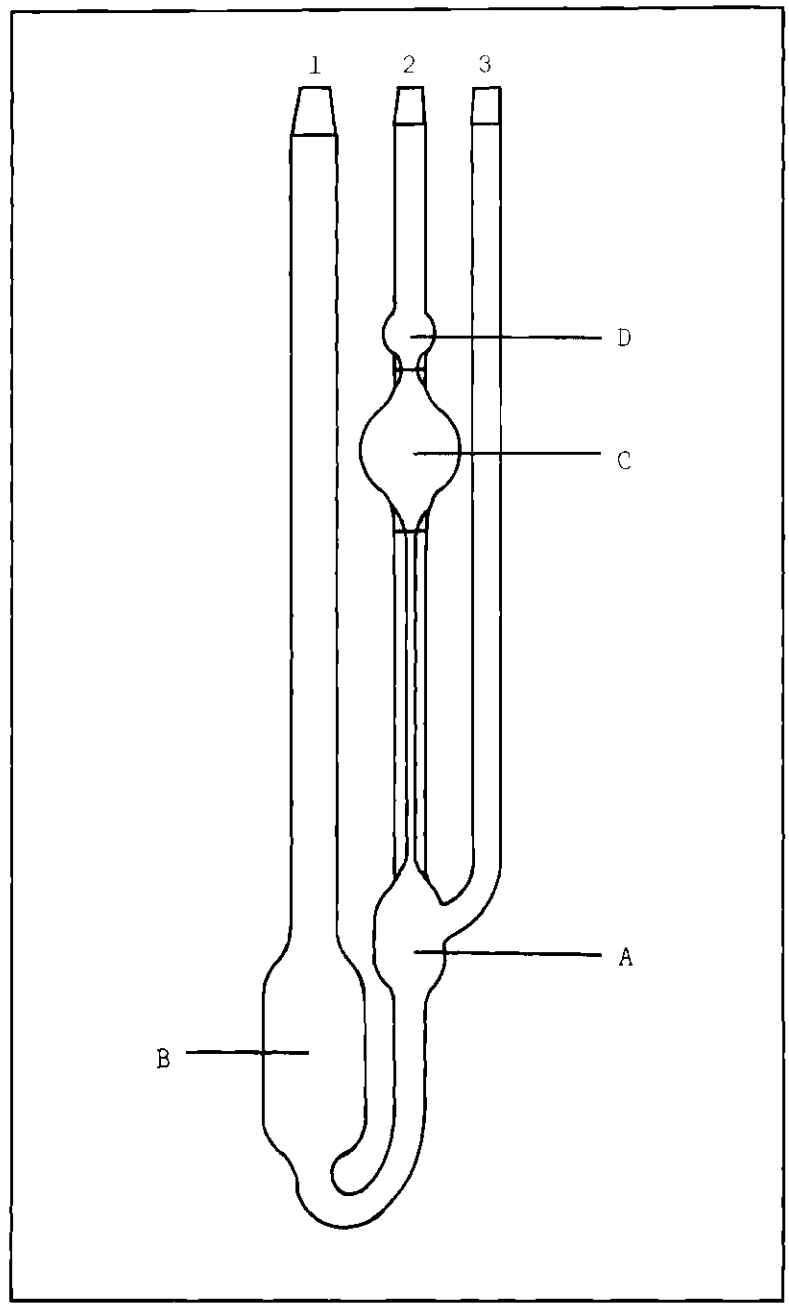


Figure 2. Ubbelohde Viscometer

the negative slope and A as the intercept on the ordinate. The calibration curve is shown in Figure 3. The values found for A and B are 9.97×10^{-3} and 1.82, respectively.

Preparation of Polymer Solution. The solutions were prepared by weighing enough polyisobutylene into 50-ml. volumetric flask to make concentrations ranging from 0.08 to 0.32 g. per 100 ml. of solution. 25 ml. of cyclohexane was added to each flask, which was agitated overnight. The polymer solutions were then dilute to the mark and were ready for the measurement.

Viscosity Measurements. 15 ml. portions of each liquid to be measured were filtered into the viscometer through the coarse glass-sintered filter, using very gentle suction. Pressure was applied to the top of bulb 1 while the top of tube 3 was closed, forcing liquid from bulb B into bulbs A and C. When bulb D was partially filled with solution, the pressure was released and the top of tube 3 was opened to the atmosphere. Flow times were taken for the liquid meniscus to pass between the two marks on bulb C. This was repeated at least four times to obtain the average flow time.

Using the calibration Equation (26), the specific viscosity was calculated and the intrinsic viscosity $[\eta]$ was determined graphically as described. Two graphical determinations of the intrinsic viscosity of both PIB L-80 and PIB L-80F are shown in Figure 4 and Figure 5, respectively.

Values of the viscosity average molecular weight $\bar{M}_v$ were calculated from Equation (22), using the values of K' and a given by Krigbaum and Flory (22). They are 7.38×10^5 for PIB L-80 and

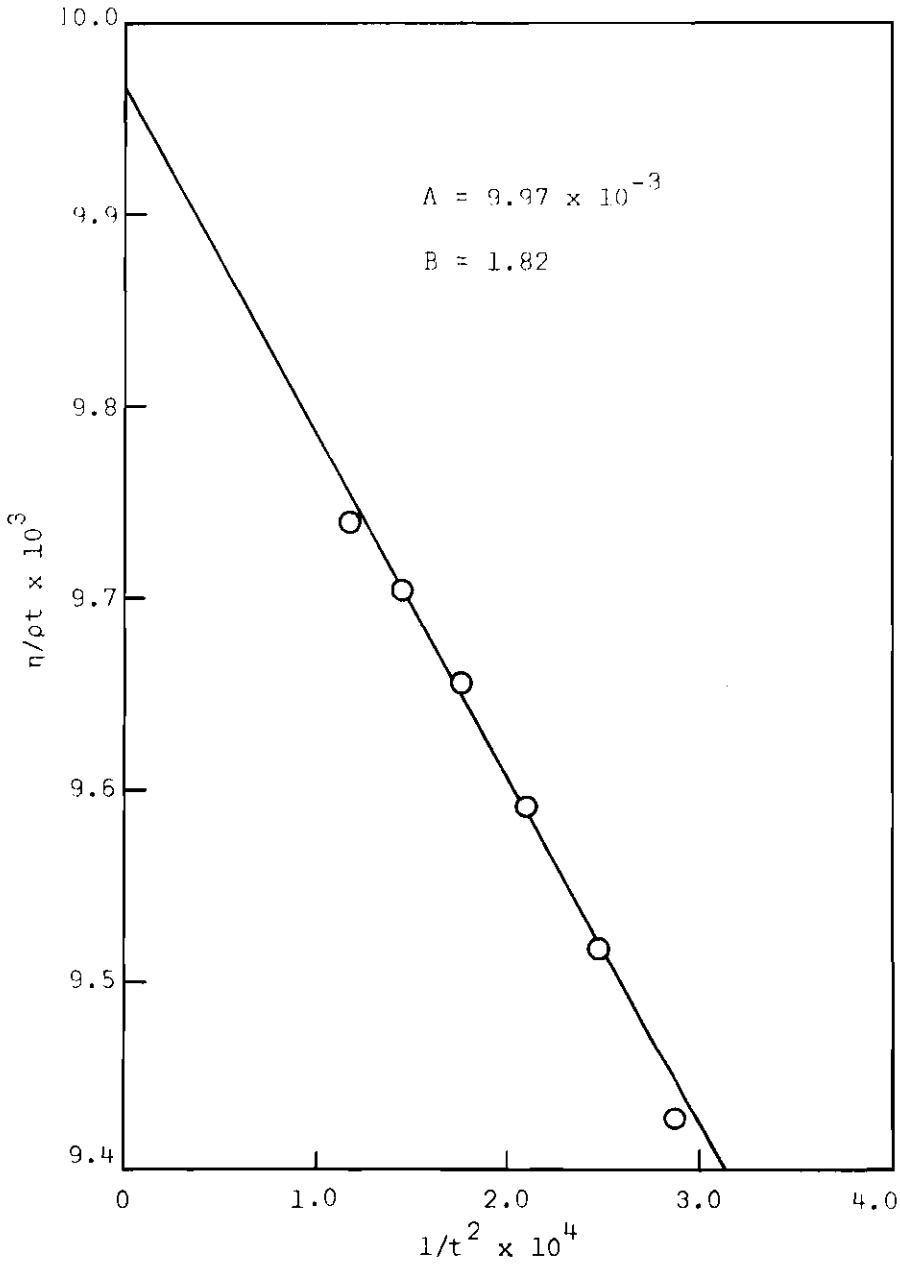


Figure 3. Viscometer Calibration Curve

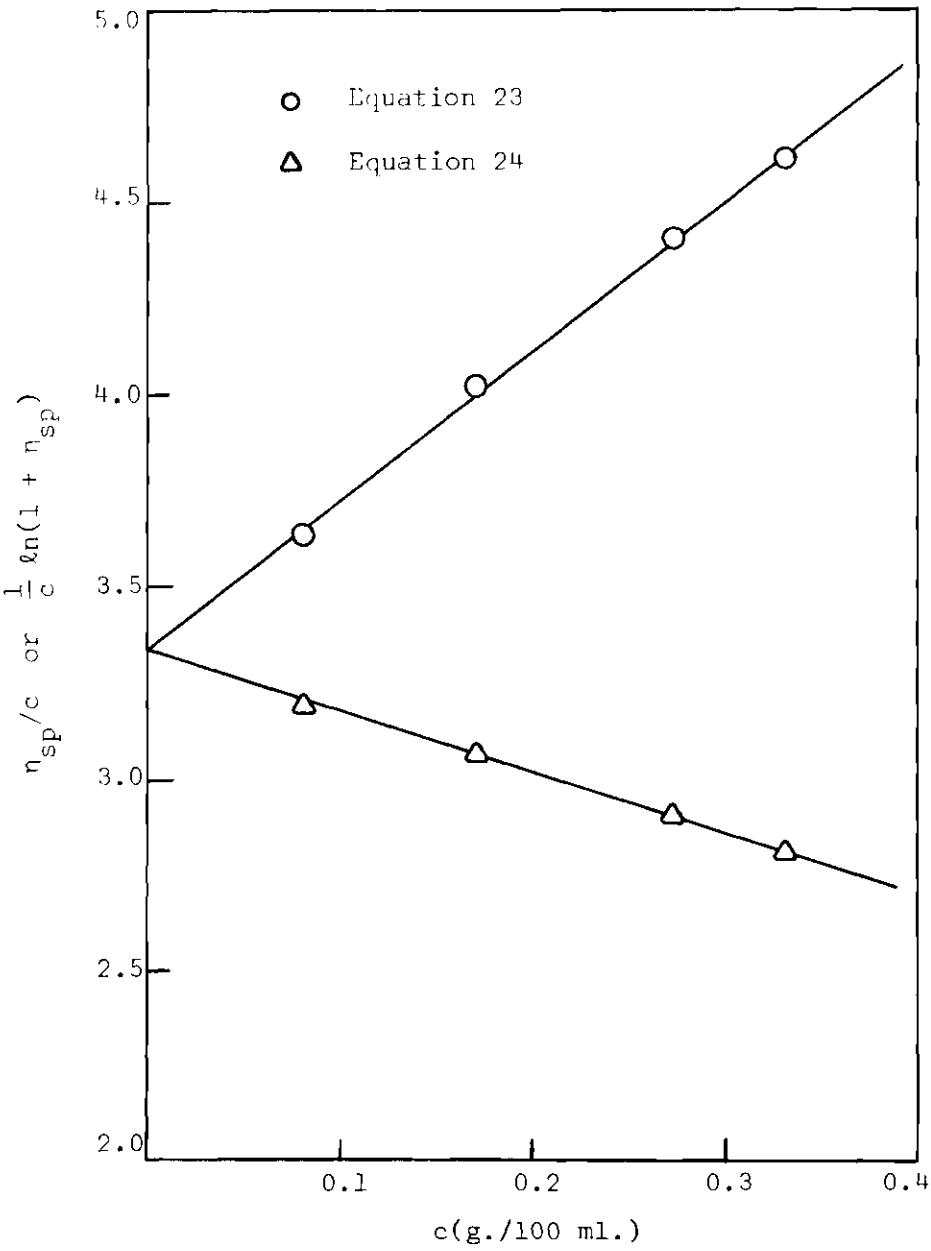


Figure 4. Determination of Intrinsic Viscosity of PIB L-80

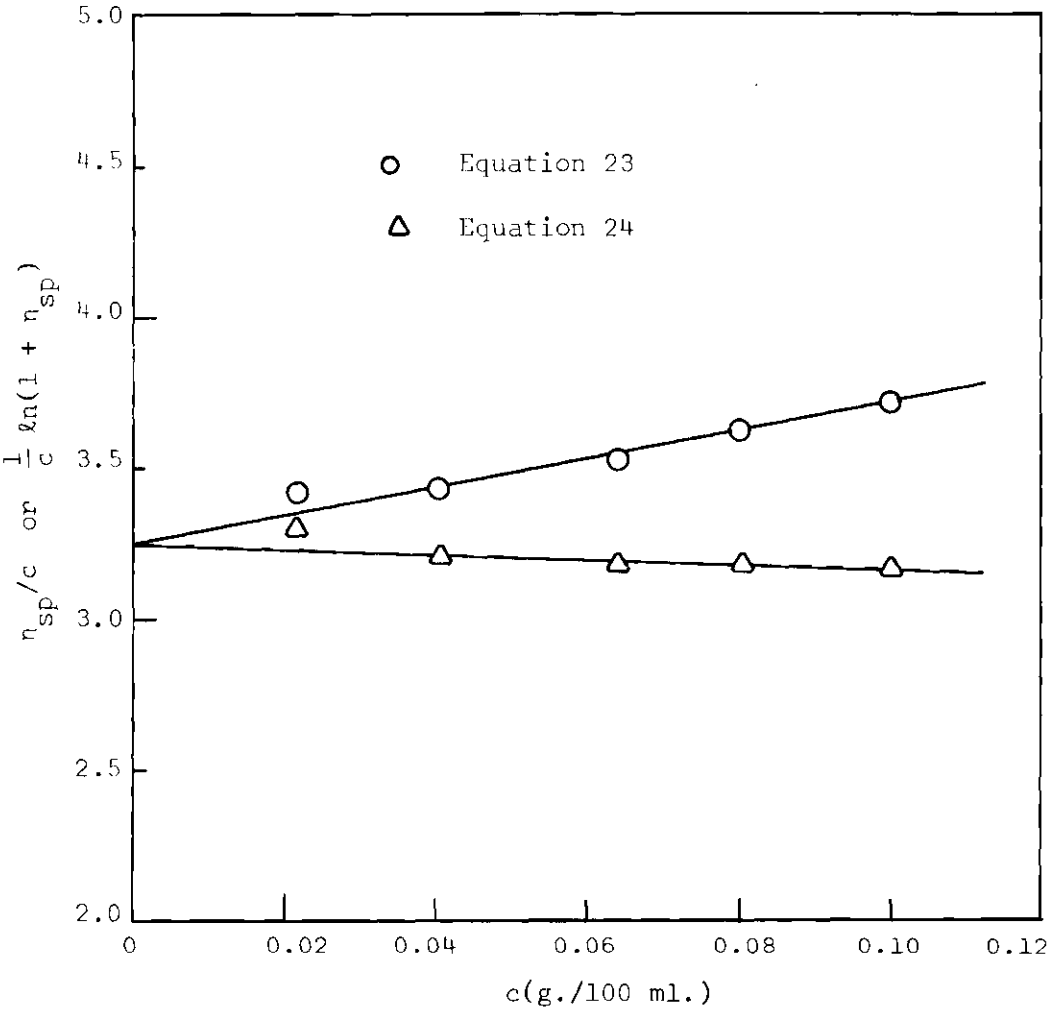


Figure 5. Determination of Intrinsic Viscosity of PIB L-80F

7.13×10^5 for PIB L-80F. Comparison of these values shows that the extent of fractionation was negligible.

Light Scattering

Light Scattering Photometer

The instrument used was a Brice-Phoenix Universal Light Scattering Photometer Series 1000 (17), made by Phoenix Precision Instrument Co. It was modified in the following manner. The Photometer was insulated inside by polystyrene foam sheets and the temperature was regulated by a blower, which supplied warm or cold air as required. One of the limit stops on the Photomultiplier Housing was bent and the shield on the removable working standard was cut off somewhat. This enabled measurements to be made over a quite wide angular range, 25° to 140°. Also the slit on the Cell-Table Diaphragm was replaced with a narrow slit of dimensions 2mm. by 6 mm.

Cell Alignment

A cylindrical light scattering cell was used for the measurements. It was lined up in the following manner. The cell was painted black with Kodak Brushing Lacquer except at the places where the incident and scattered lights would go through. It was then washed with cleaning solution and rinsed with distilled water. After drying, it was washed again by the condensing vapor of methanol in special device constructed for this purpose (25). The outside was cleaned with a silicone cloth.

50 ml. of methanol solution containing a trace of fluorescein dye in an amount sufficient to give a slight greenish color was filtered

under the nitrogen pressure into the cell through a fine glass-sintered filter. The cell was then placed on the cell table. The mercury blue line at 4358 Å was allowed to fall on the solution. The voltage was then adjusted so that the galvanometer reading at 25° angle was near full scale. Readings were taken from 25° to 140° at 5° intervals. The cell was moved about on the table until it was found that the galvanometer readings were symmetrical about the 90° angle or a constant value was obtained when the galvanometer reading was multiplied by the sine of that angle. Then the cell was considered to be lined up. The cell was then glued to its base, using the Elmer's Glue-All. Redistilled benzene was used to check the alignment using the following equation

$$G(\theta)/G(90) = \left(\frac{1}{\sin\theta}\right)\left[1 + (1 - \rho)\cos^2\theta/(1 + \rho)\right] \qquad (27)$$

where ρ is the depolarization of benzene at 90° (26). The precision of the cell alignment was within ±3.0 per cent.

Preparation of Solution for Light Scattering Measurement

Dust and impurities in the solvent affect greatly the intensity of the scattered light. Hence solutions were carefully prepared so that they would be free of dust.

Polymer solutions were prepared by making up given concentrations ranging from 0.03 to 0.12 g. per 100 ml. solution (0.08 to 0.32 g. per 100 ml. solution in the case of atactic PMMA solution). Four solutions were prepared for each experiment. Each solution was filtered through an ultrafine glass-sintered filter into the cleaned cell. The filter was thoroughly cleaned with cleaning solution, dried, and rinsed several

times with solvent before using.

Mixed solvents of known volume fractions were prepared at room temperature by mixing appropriate weight of solvents, the densities of which were known.

At higher compositions of non-solvent it was necessary to warm up the solutions during the filtration process, to prevent clogging of the filter by polymer. When filtering solutions of PMMA a Tesla vacuum tester was used to charge the filter electrically during the filtration process, since it was discovered that it helped considerably to produce dust-free liquids. If necessary, several passes through the filter were made.

Light Scattering Measurements

The cell was covered with a glass plate and positioned in the photometer after filtering. By looking through the solution at an angle close to the transmitted beam, the presence of any residual dust was apparent. In such cases filtration was repeated until no bright specks were visible.

Before readings were taken, ten minutes were allowed to reach temperature equilibrium. Unpolarized mercury light of 4358 Å or 5461 Å was used. The phototube was moved to 25°. The voltage was turned up high enough so that the galvanometer reading at that angle was near full scale. Galvanometer readings were taken from 25° to 140° at 5° intervals. After every four readings had been taken, the phototube was turned back to 25° to check for constancy of voltage applied to the photomultiplier tube. The galvanometer reading at zero degree angle was also taken. Since the intensity of the transmitted

beam was very high, certain combinations of neutral filters were required for attenuation. The reading at 0° was made three times and the average was taken.

After the angular measurements were completed, exactly 25 ml. of each solution were evaporated to dryness in an aluminum pan and weighed to determine the exact concentration of the solution.

Treatment of Light Scattering Data

The intensity of the scattered light is proportional to the galvanometer reading. When unpolarized light is used, the following equation gives the apparent intensity in galvanometer units:

$$R'_\theta = G(\theta) \frac{T}{G(\theta)} \frac{\sin \theta}{1 + \cos^2\theta} \tag{28}$$

where θ is the angle between scattered light and the incident light, $G(\theta)$ is the galvanometer reading at that angle, $G(0)$ is the reading at the zero angle, and T is the transmittance of the neutral filter combination used at zero degrees. Since a portion of the incident beam is reflected back into the cell at the exit face, the true intensity of scattered light in galvanometer units is

$$R''_\theta = R'_\theta - xR'_{180-\theta}$$

where x is the fraction of the light reflected back into the solution. The value of x can be calculated from the following equation:

$$x = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

where n_1 and n_2 are refractive indices of benzene and Pyres glass, respectively. The difference of the intensities of the scattering of the solution and the solvent, the excess intensity, must be converted to absolute units. The standard used for this purpose was benzene (27), for which was adopted the value of 4.65×10^{-5} cm^{-1} for the Rayleigh ratio at 20° C and 4358 Å (or 1.56×10^{-5} cm^{-1} at 20° C and 5461 Å). The temperature dependence of the Rayleigh ratio (28) is:

$$R_t/R_{25} = 1 + 0.368 \times 10^{-2} (t - 25)$$

The following relation was used to calculate the excess intensity R_θ:

$$R_\theta = (\text{Rayleigh ratio of benzene}) \times \frac{R''_\theta}{R'_{90}}$$

where R'_{90} is intensity of scattered light of benzene at 90° angle. For the macromolecular solution c/R_θ varies with angle, so c/R_θ was calculated for each angle. To construct Zimm plots, Kc/R_θ was plotted versus $kc + \sin^2\theta/2$, where K is the optical constant defined in Equation (10) in the first chapter and k is a constant chosen to spread out the experimental data. Using this plot for extrapolations, the zero concentration and the zero angle lines meet at a common intercept. Extrapolating to zero concentration at $\theta = 0°$, a plot of Kc/R_o versus kc

was obtained. The initial slope of this line gives the second virial coefficient, A_2. Since the destructive interference vanishes at the zero degree angle, $P(\theta)$ of the Equation (16) becomes unity. Therefore the intercept of this line gives the value of $\bar{M}_w$; i.e., $\bar{M}_w$ is the reciprocal of the intercept. Extrapolating to zero angle at c = 0, there is obtained a plot of Kc/R_θ versus $\sin^2\theta/2$. $P(\theta)$ is related to the radius of gyration, which is root-mean-square distance of the elements of the chain from its center of gravity, by the following equation

$$1/P(\theta) = 1 + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2\theta/2 + \ldots \qquad (30)$$

Thus Equation (16) becomes

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{\bar{M}_w}\left(1 + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2\theta/2 + \ldots\right) \qquad (31)$$

The slope of this line gives the radius of gyration and the intercept gives the reciprocal of weight average molecular weight.

The light scattering data were treated in this manner except for the atactic PMMA-acetone-cyclohexane system, where only a Kc/R_o versus c plot was constructed.

Specific Refractive Index Increment $(dn/dc)_T$

The specific refractive index increment $(dn/dc)_T$ must be known to calculate the weight average molecular weight. No such values are reported in the literature for systems containing PIB. The measurement

of this quantity can not be made with an ordinary refractometer, for the refractive index difference between the solvent and the polymer solution is too small to permit the difference to be measured with sufficient precision. A Brice-Phoenix Visual Differential Refractometer Model BP-1000-V (29) was therefore used for this measurement. The precision in the measurement of Δn with this instrument is $\pm 3.0 \times 10^{-6}$.

Calibration of Differential Refractometer

A sodium lamp was used. Pure sucrose solutions were used for the calibration. The refractive index of sucrose solutions are given in the literature (30). Both compartments of the cell were filled with 1 ml. of distilled water. Ten minutes were allowed for temperature equilibrium. With one side of the cell toward the lamp, the microscope was focused until a clear line was obtained. The hair line was set at the center of the line. The reading from the micrometer drum was recorded as d_1. The same procedure was repeated with the cell turned through an angle of 180°. This reading was recorded as d_2. Readings were made four times and the mean values were taken. $(d_1 - d_2)_{solvent}$ is the zero reading for the pure solvent. One ml. each of 2, 4, 5 and 6 per cent sucrose solutions (by weight) was introduced into the solution cell. $(d_1 - d_2)$ for each of these solutions was determined in the same way as for the solvent. The total displacement is defined as:

$$\Delta d_T = (d_1 - d_2)_{solution} - (d_1 - d_2)_{solvent} \equiv \Delta n/K \qquad (31)$$

When the refractive index difference between solution and the solvent Δn is plotted against total displacement Δd_T, a straight line is

obtained with slope K, the calibration constant for the sodium D line. The calibration curve is shown in Figure 6. The calibration constants for different wavelengths are related to each other by the following equation (31)

$$K_\lambda = K_{5893} \, (M_{5893}/M_\lambda) \tag{32}$$

The values of M_{5893} and M_λ were given for the instrument in the manufacturer's instruction manual.

Measurement of $(dn/dc)_T$ for PIB in Cyclohexane-Acetone

Measurements of $(dn/dc)_T$ were made at 35°C and 25°C for the solutions of PIB in pure cyclohexane. Only one successful measurement was performed at 35°C for the PIB-mixed solvent system, at an acetone concentration of 10 per cent by volume. Unpolarized incident radiation of 4358 Å and 5461 Å were used. The total displacement for each system was made by following the same procedure described in calibration section. The refractive index difference Δn was obtained by multiplying the total displacement Δd_T by the calibration constant K. When Δn was plotted against solution concentration c, a straight line was obtained with slope equal to the specific refractive index increment $(dn/dc)_T$. Results are tabulated and are shown in Appendices 1 to 12.

Calculation of $(dn/dc)_T$ in the Mixed Solvent

Measurements of $(dn/dc)_T$ were unsatisfactory when the volume fraction of acetone was greater than 0.10 because of evaporation problems. It was therefore decided to calculate such values from the Lorenz-Lorentz equation. However, the value of the refractive index

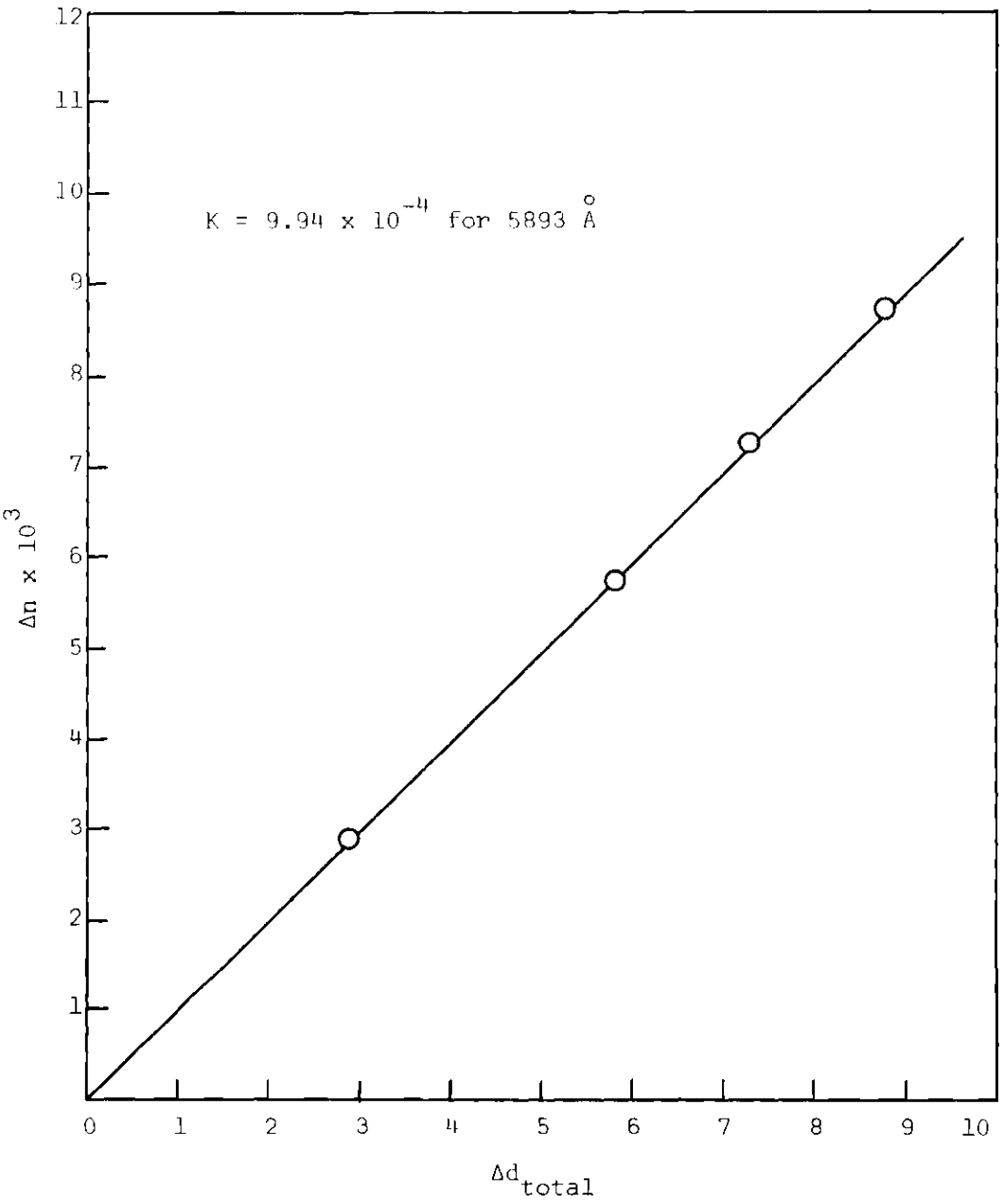


Figure 6. Calibration of Differential Refractometer

of PIB at the desired wavelength was unknown. Using the Lorenz-Lorentz equation, the numerical value of refractive index of PIB was adjusted so that the calculated values of $(dn/dc)_T$ at 0 per cent and 10 per cent of acetone gave the best agreement with our experimental measurements.

The specific refraction R_i is

$$R_i = \left(\frac{1}{d_i}\right)\left(\frac{n_i^2 - 1}{n_i^2 + 2}\right) \tag{33}$$

where d_i is the density at the same temperature to which the value of n_i applies. The specific refraction of a binary mixture R may be written

$$R = w_1R_1 + w_2R_2 \tag{34}$$

where w_1 and w_2 are the weight fractions of component 1 and 2, respectively. Denoting by w_2d the concentration c of the component 2 and assuming the additivity of volumes, Equation (35) is obtained

$$\frac{n^2 - 1}{n^2 + 2} = \frac{c}{d_2}\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) + \left(1 - \frac{c}{d_2}\right)\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) \tag{35}$$

where n_1 and n_2 are the refractive indices of the components 1 and 2, respectively, and n is the refractive index of the binary mixture. If Equation (35) is differentiated with respect to c, the following expression is obtained

$$(dn/dc)_T = \frac{(n^2 + 2)}{6n}\left[\frac{1}{d_2}\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) - \frac{1}{d_2}\left(\frac{n_1^2 - 1}{n_2^2 + 2}\right)\right] \qquad (36)$$

On the polymer-pure solvent system, 1 refers to solvent and 2 refers to polymer. Then $(dn/dc)_T$ was calculated directly from Equation (36) by knowing n (refractive index of the solution) from Equation (35). When the mixed solvent was used, the refractive index of the mixed solvent was calculated first from Equation (35) and the resulting value was considered to be that of 1. Using the same equation (Equation (35)), the refractive index for the polymer solution in the mixed solvent was calculated, and this value was then used in Equation (36) to calculate $(dn/dc)_T$.

The specific refractive index increment at various compositions of non-solvent for the PMMA-acetone-cyclohexane system was also calculated in the same manner, assuming that the refractive index and density are the same for atactic and syndiotactic samples.

The quantity $(dn/dv_1)_{c_3=0}$, which is required in the calculation of the selective adsorption constant α, can be written:

$$(dn/dv_1)_{c_3=0} = - d_2(dn/dc_2)_{c_3=0}$$

where $(dn/dc_2)_{c_3=0}$ was calculated from Equation (36).

The required densities and refractive indices of the solvents at different temperature and wavelength were found in literature (32,33). These are shown in Appendices 13 to 16, from which the densities and refractive indices at desired temperatures and wavelengths were found.

The refractive indices and densities for the polymers and solvents at the appropriate temperatures are summarized in Appendix 17.

The results of the calculations of $(dn/dc)_T$ are shown in Appendices 18 to 22.

CHAPTER III

RESULTS AND DISCUSSION

For each run on PIB and syndiotactic PMMA systems, a Zimm plot was constructed. Figures 7 to 10 show such plots for the system PIB-cyclohexane-acetone at 4358 $\mathring{A}$, where the volume fraction of acetone was 0.00, 0.10, 0.15 and 0.20. Figure 11 shows the data obtained for the system PIB-cyclohexane-benzene at 4358 $\mathring{A}$ for the case 0.20 volume fraction of benzene. For the atactic PMMA-acetone-cyclohexane system, a plot of Kc/R_o versus c was constructed. The plots of Kc/R_o versus c for PIB, syndiotactic and atactic PMMA systems are shown in Figures 12, 13 and 14, respectively. The selective adsorption of the mixed solvent is reflected by the change of the apparent weight average molecular weight $\bar{M}_w^*$, which was used to calculate the adsorption constant from Equation (15). The results are shown in Tables 1 to 5.

Tables 6 and 7 show the values of the second virial coefficients A_2 and the radii of gyration R_G for these systems, calculated from the slope of zero angle and of zero concentration of Zimm plot, respectively. The second virial coefficient and radius of gyration as a function of solvent power at 4358 $\mathring{A}$ are shown in Figures 15 and 16 for the systems PIB-cyclohexane-acetone and syndiotactic PMMA-acetone-cyclohexane, respectively.

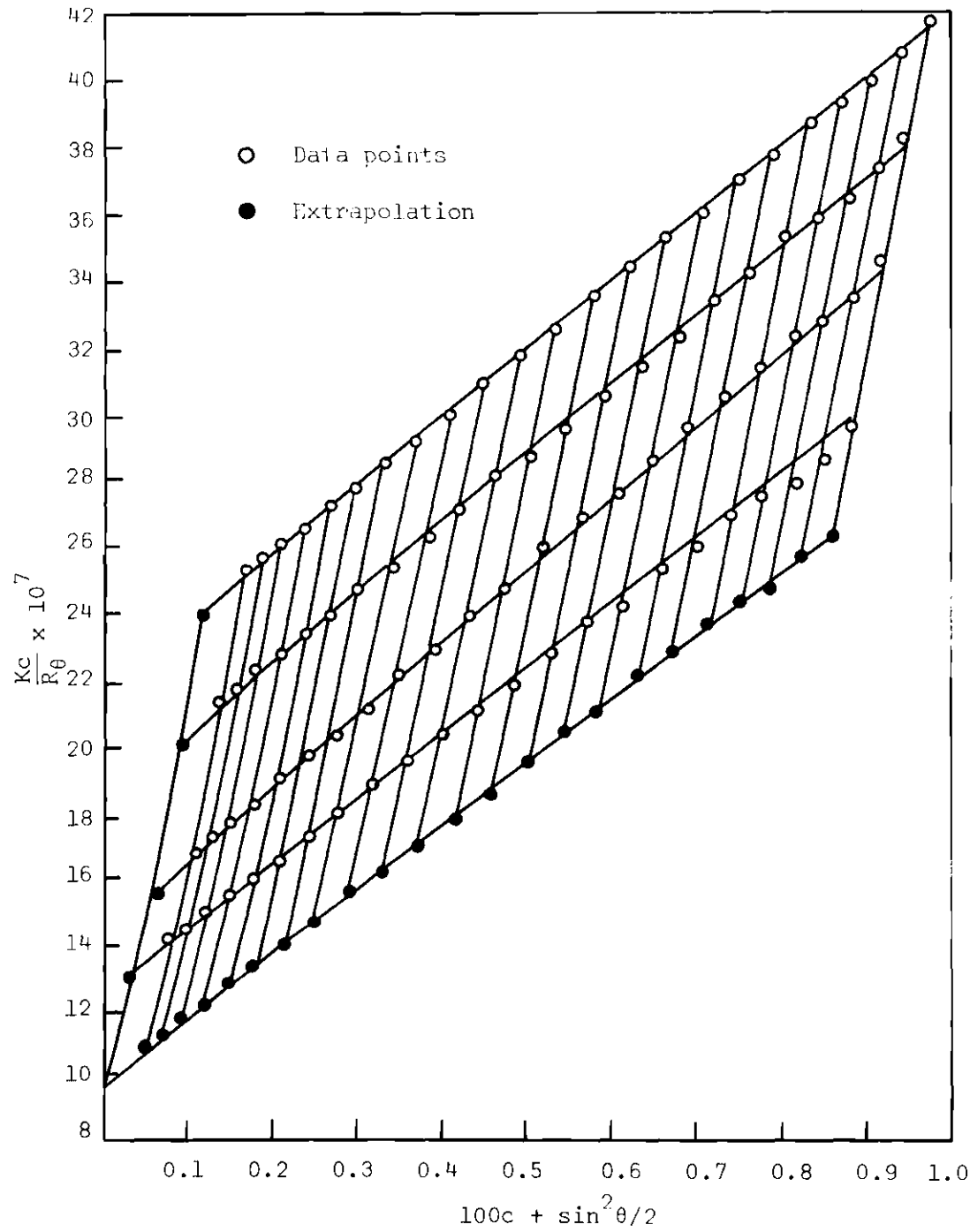


Figure 7. Zimm Plot for PIB L-80F in Cyclohexane at 35°C and 4358 Å

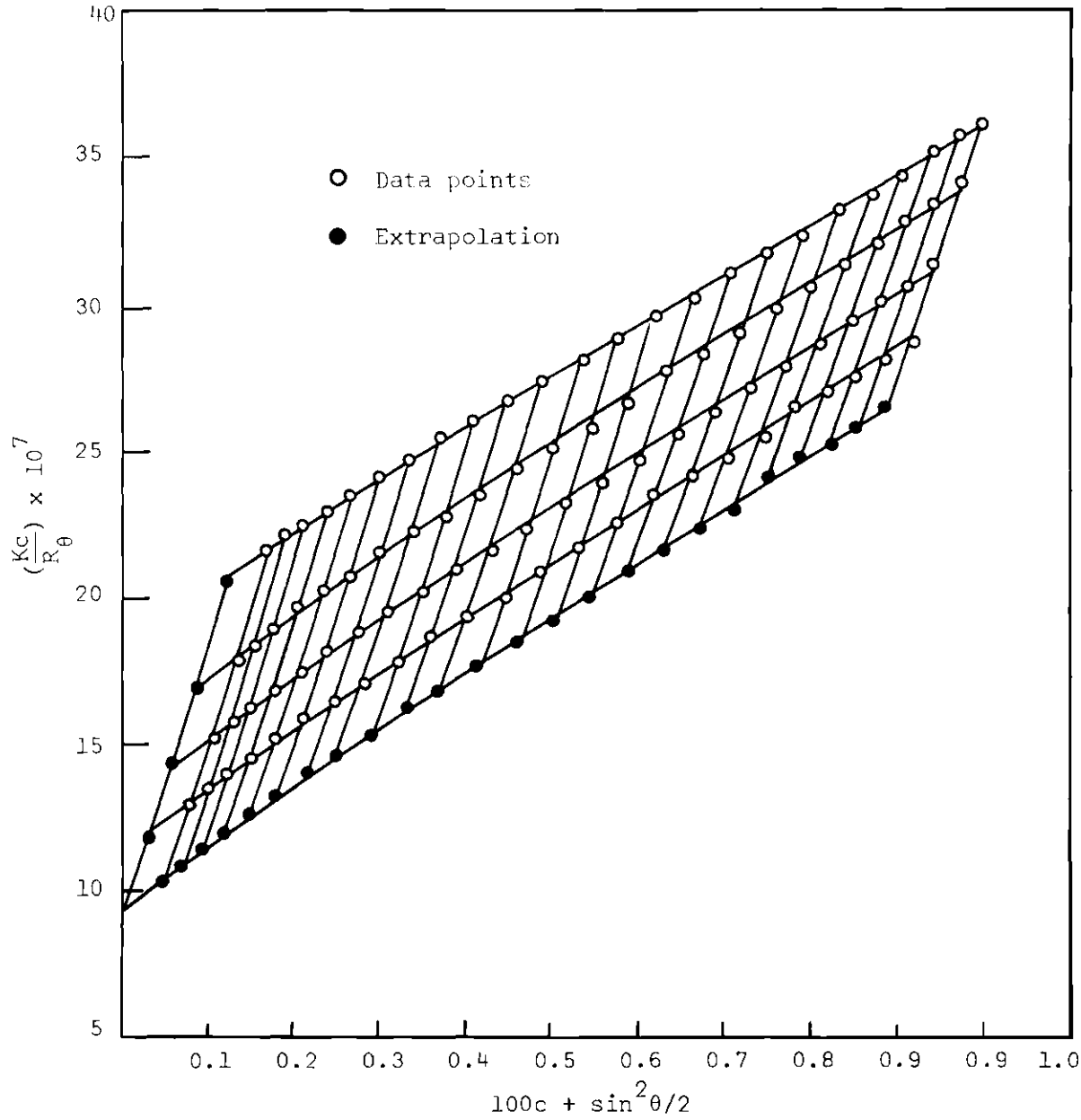


Figure 8. Zimm Plot for PIB L-80F in 10 Per Cent of Acetone at 35°C and 4358 Å

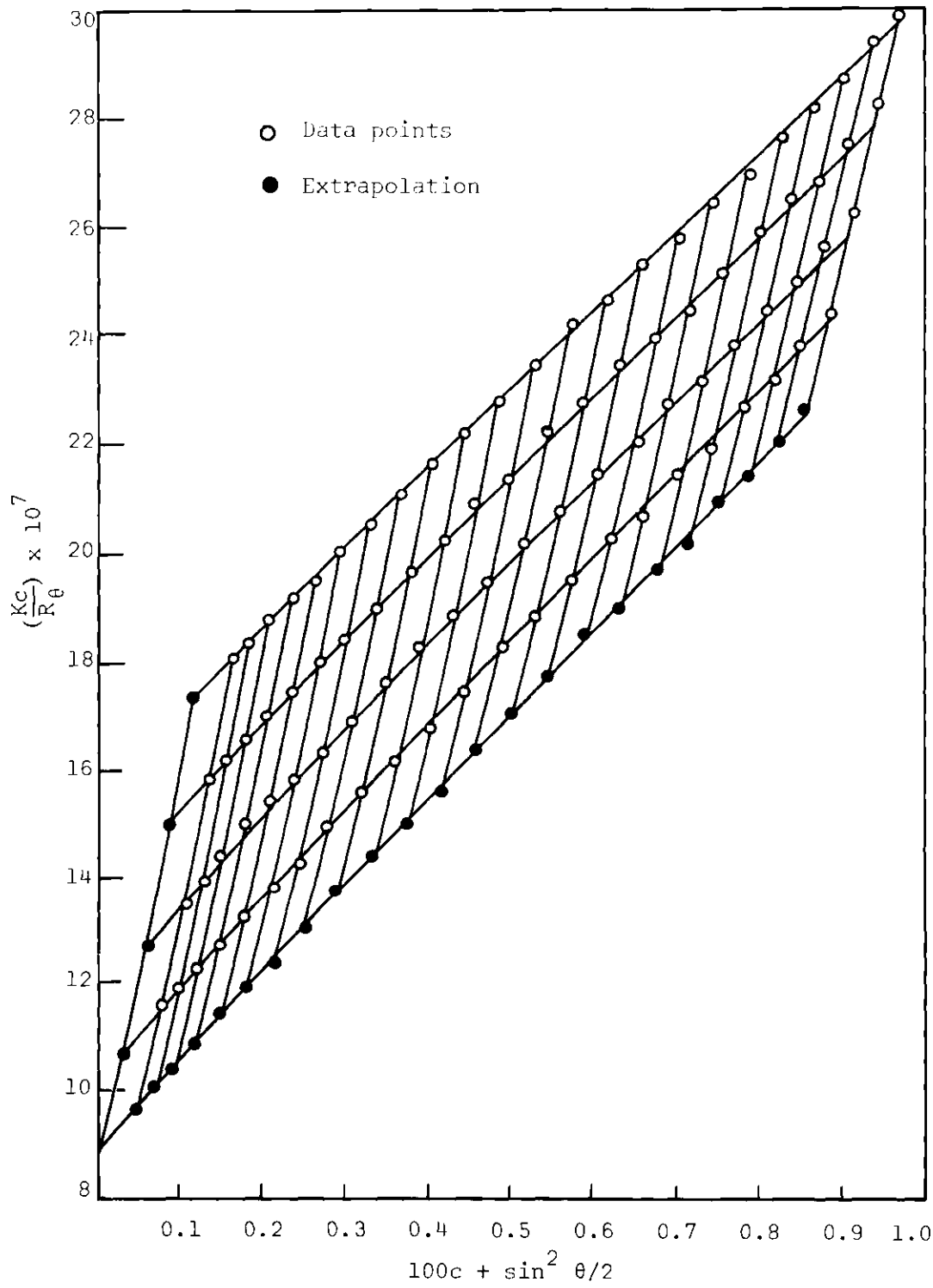


Figure 9. Zimm Plot for PIB L-80F in 15 Per Cent of Acetone at 35°C and 4358 Å

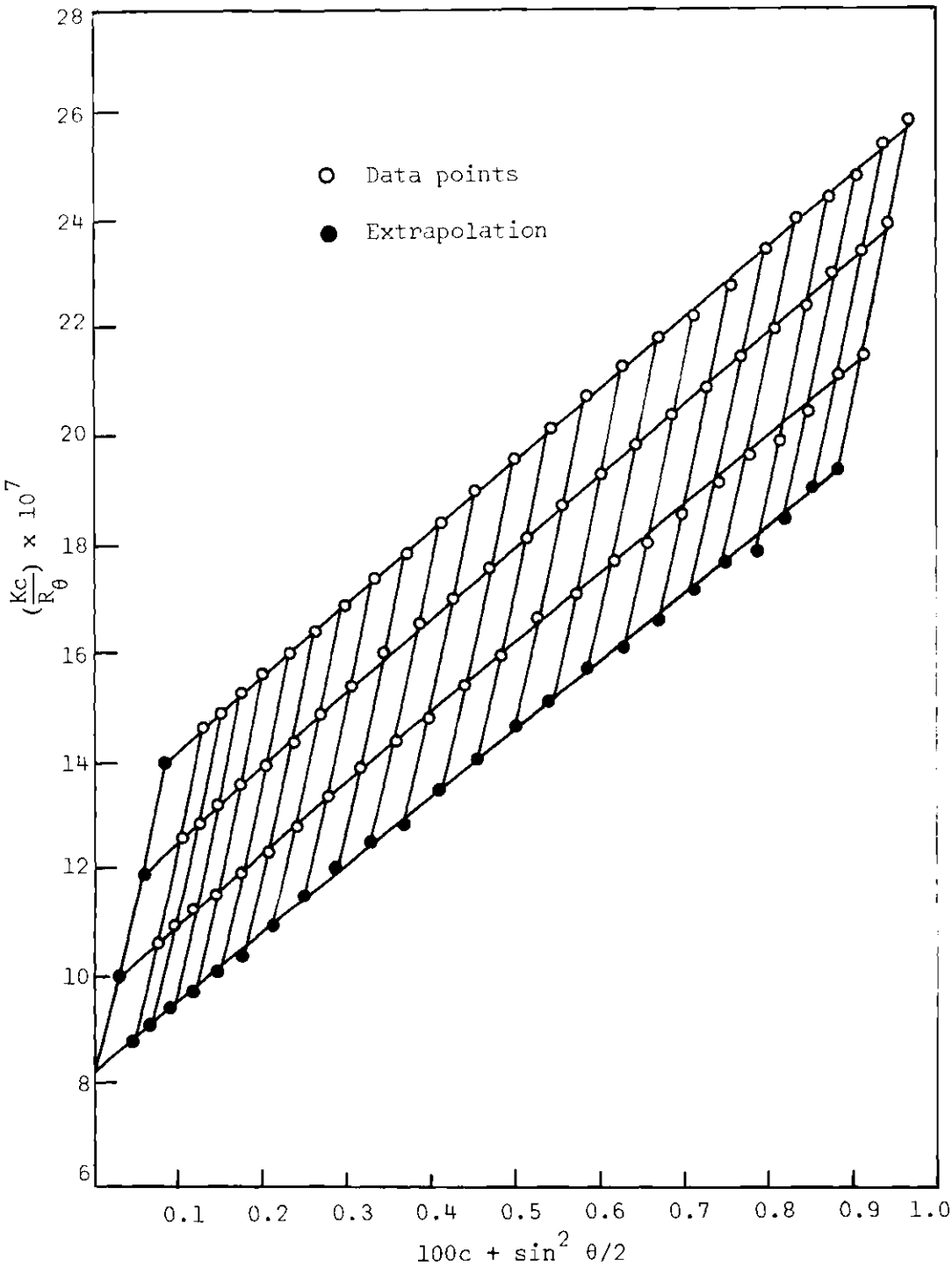


Figure 10. Zimm Plot for PIB L-80F in 20 Per Cent of Acetone at 35°C and 4358 Å

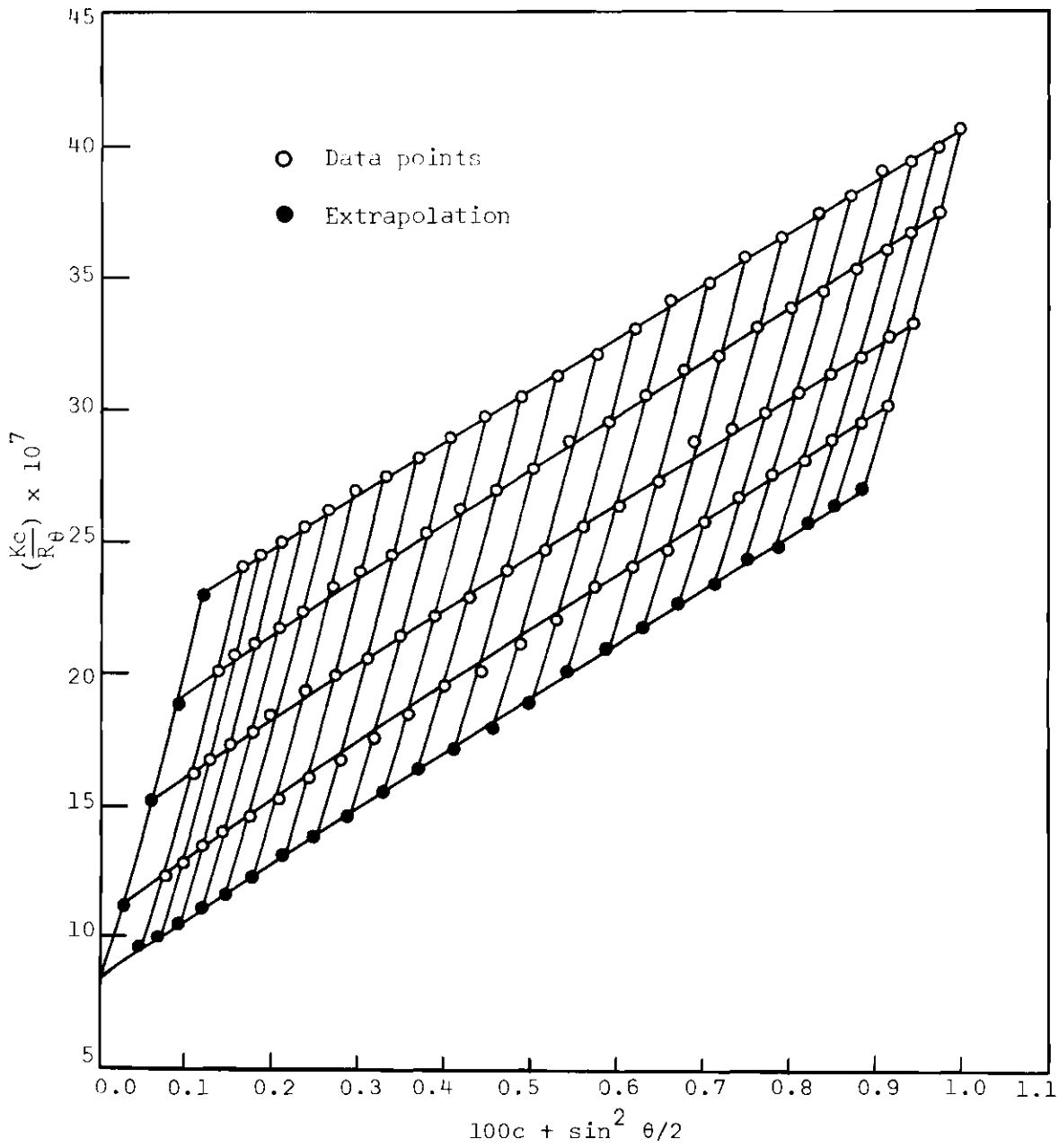


Figure 11. Zimm Plot for PIB L-80F in 20 Per Cent of Benzene at 25°C and 4358 Å

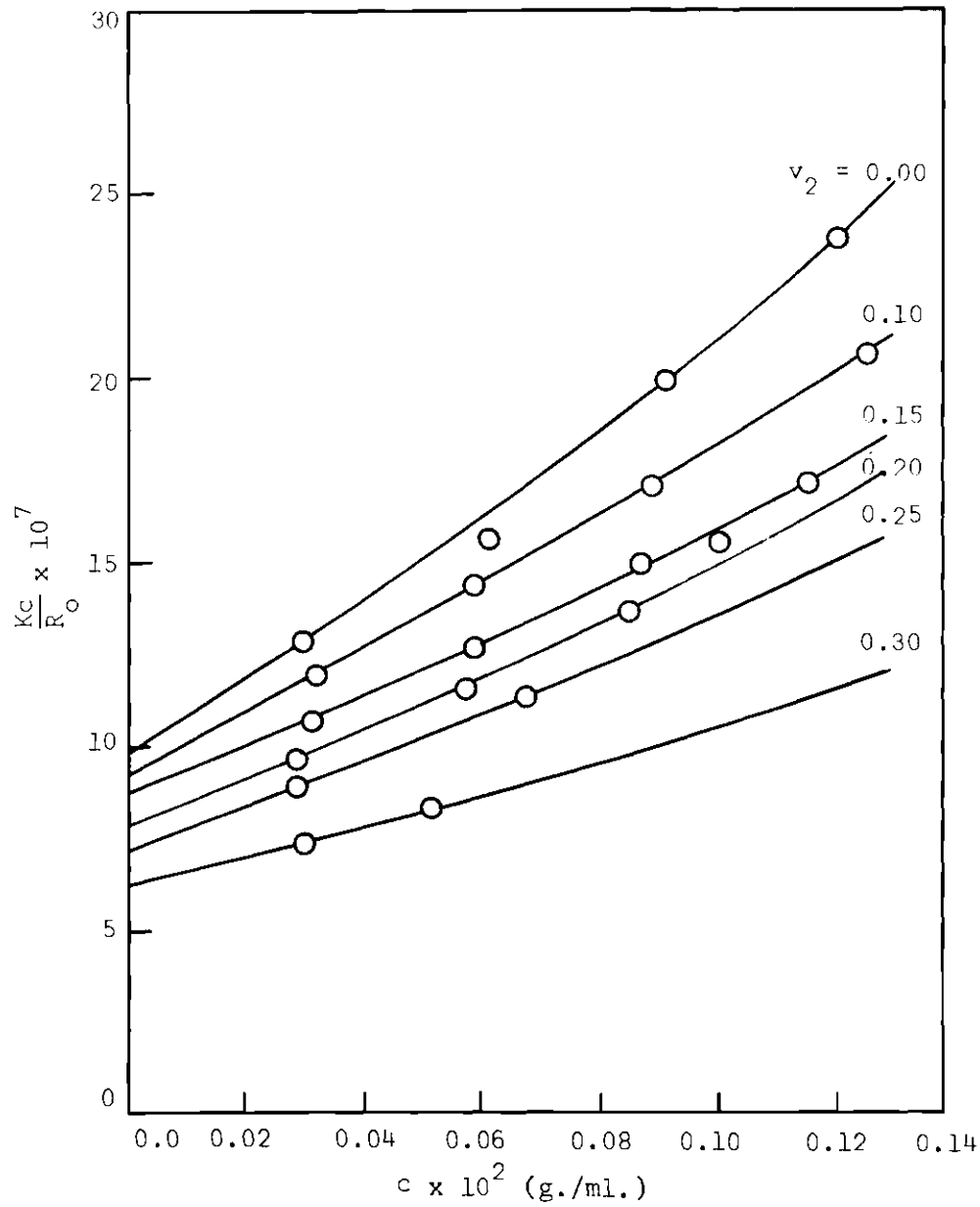


Figure 12. The (Kc/R_o)-Concentration Relations Obtained from Zimm Plot for PIB L-80F in Cyclohexane-Acetone Mixtures at 35°C and 4358 Å

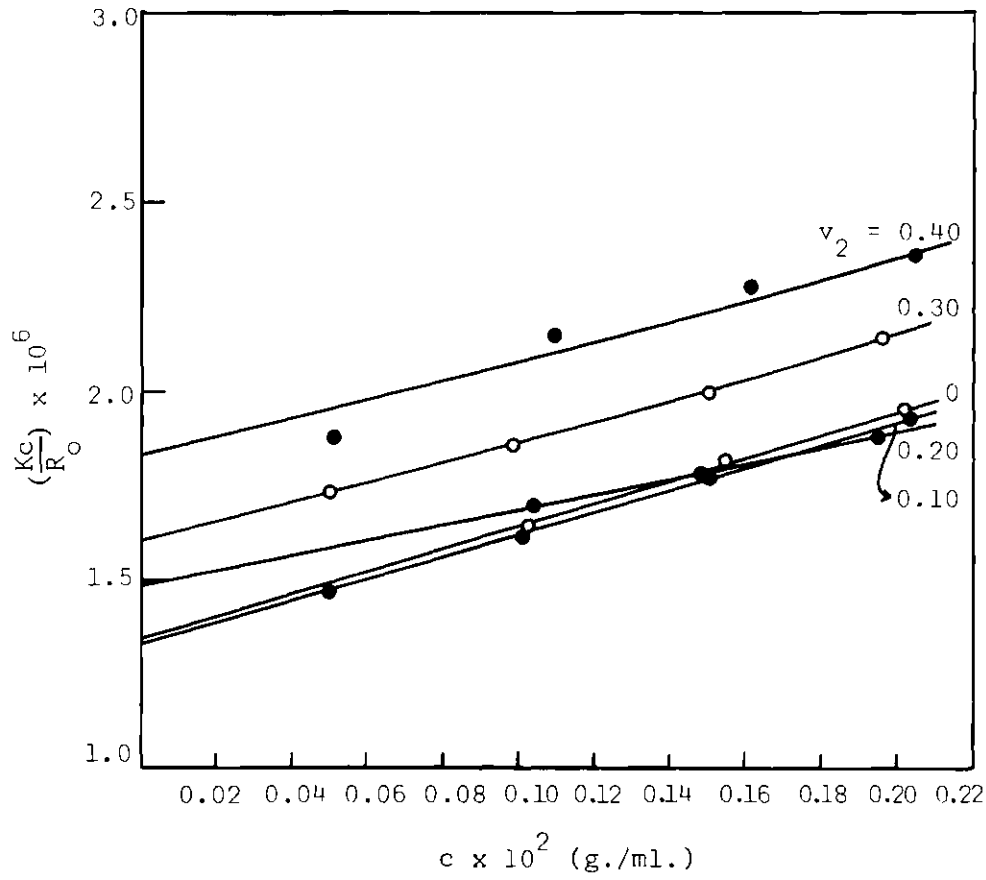


Figure 13. The (Kc/R_o)-Concentration Relations Obtained from Zimm Plot for Syndiotactic PMMA in Acetone-Cyclohexane Mixtures at 25°C and 4358 Å

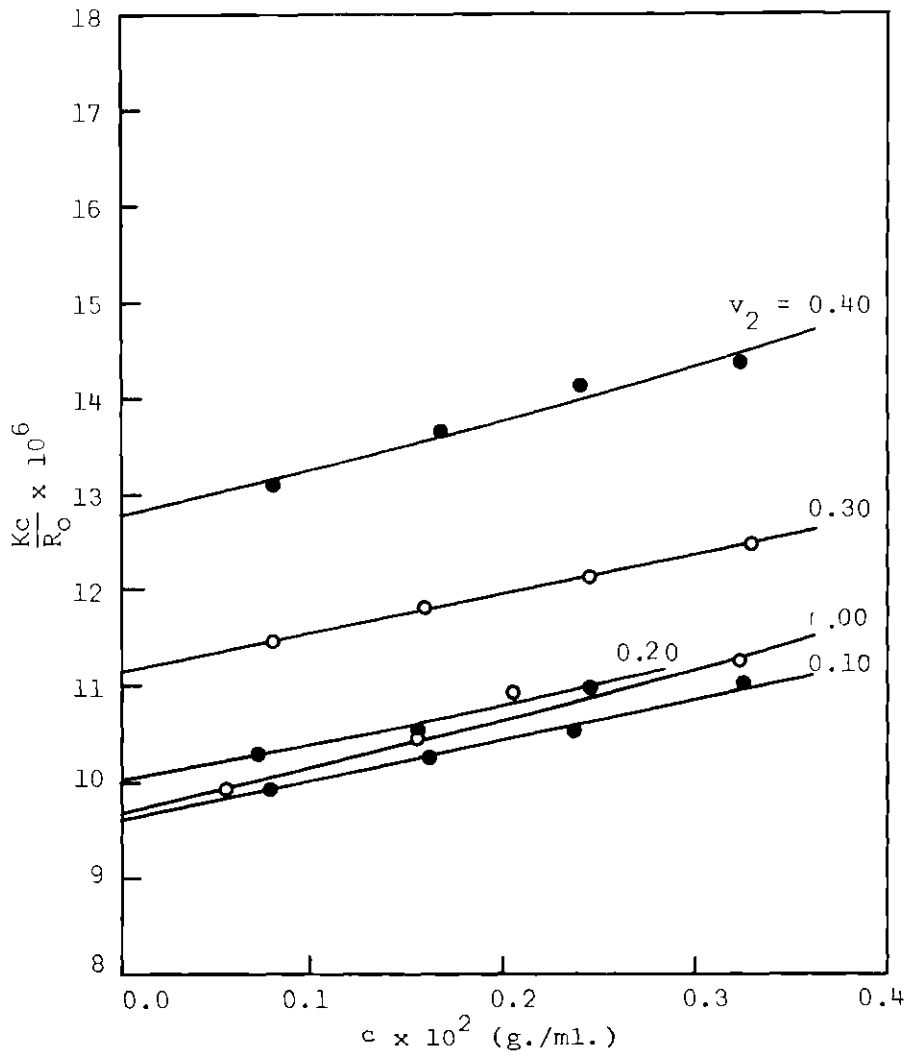


Figure 14. The (Kc/R_o)-Concentration Relations Obtained from Zimm Plot for Atactic PMMA in Acetone-Cyclohexane Mixtures at 25°C and 4358 Å

Table 1. Experimental Results of Adsorption Constant α_o for PIB-Cyclohexane-Acetone at 35°C and 4358 Å

Vol. Fraction of Acetone	$Kx10^7$	(c/R''_θ)	$K\frac{c}{R''_\theta}(\frac{R'_{90}}{R_{90}})x10^7$	$\bar{M}_w$ or $\bar{M}^*_w x10^{-6}$	α
$v_2 = 0.00$	2.08	0.0381	9.73	1.03	0.0000
$v_2 = 0.10$	2.38	0.0315	9.20	1.09	0.047±0.03
$v_2 = 0.15$	2.48	0.0288	8.76	1.14	0.092±0.03
$v_2 = 0.20$	2.61	0.0242	7.76	1.29	0.212±0.05
$v_2 = 0.25$	2.75	0.0212	7.15	1.40	0.302±0.06
$v_2 = 0.30$	2.89	0.0172	6.11	1.64	0.490±0.05

Table 2. Experimental Results of Adsorption Constant α_o for PIB-Cyclohexane-Acetone at 35°C and 5461 Å

Vol. Fraction in Acetone	$Kx10^8$	(c/R''_θ)	$K\frac{c}{R''_\theta}(\frac{R'_{90}}{R_{90}})x10^7$	$\bar{M}_w$ or $\bar{M}^*_w x10^{-6}$	α
$v_2 = 0.00$	8.16	0.0617	5.29	1.89	0.0000
$v_2 = 0.10$	9.16	0.0510	4.91	2.04	0.062±0.03
$v_2 = 0.15$	9.71	0.0466	4.76	2.10	0.093±0.04
$v_2 = 0.20$	10.24	0.0370	3.99	2.51	0.267±0.05
$v_2 = 0.25$	10.79	0.0324	3.68	2.72	0.362±0.06
$v_2 = 0.30$	11.34	0.0270	3.22	3.11	0.526±0.05

Table 3. Experimental Results of Adsorption Constant for PIB in 20 Per Cent of Benzene at 25°C

λ, Å	v_2	$Kx10^8$	(c/R''_θ)	$K\frac{c}{R''_\theta}(\frac{R'_{90}}{R_{90}})x10^7$	$\bar{M}_w$ or $\bar{M}^*_w x10^{-6}$	α
4358	0.00	18.97	0.0416	9.68	1.04	0.0000
4358	0.20	13.31	0.0519	8.47	1.18	-0.068±0.03
5461	0.00	7.43	0.0636	4.97	2.01	0.0000
5461	0.20	5.42	0.0783	4.47	2.24	-0.062±0.03

Table 4. Experimental Results of Adsorption Constant α for Syndiotactic PMMA-Acetone-Cyclohexane at 25°C and 4358 Å

Vol. Fraction of Cyclohexane	$Kx10^7$	(c/R''_θ)	$K\frac{c}{R''_\theta}(\frac{R'_{90}}{R_{90}})x10^6$	$\bar{M}_w$ or $\bar{M}^*_w x10^{-5}$	α
$v_2 = 0.00$	3.14	0.0353	1.35	7.41	0.0000
$v_2 = 0.10$	2.94	0.0371	1.33	7.51	-0.013±0.01
$v_2 = 0.20$	2.74	0.0446	1.46	6.85	0.073±0.03
$v_2 = 0.30$	2.55	0.0514	1.60	6.26	0.146±0.03
$v_2 = 0.40$	2.36	0.0609	1.83	5.47	0.242±0.03

Table 5. Experimental Results of Adsorption Constant α for Atactic PMMA-Acetone-Cyclohexane at 25°C and 4358 Å

Vol. Fraction of Cyclohexane	$Kx10^7$	(c/R''_θ)	$K\frac{c}{R''_\theta}(\frac{R'_{90}}{R_{90}})x10^6$	$\bar{M}_w$ or $\bar{M}^*_w x10^{-5}$	α
$v_2 = 0.00$	3.14	0.252	9.65	1.036	0.0000
$v_2 = 0.10$	2.94	0.268	9.60	1.042	-0.005±0.01
$v_2 = 0.20$	2.74	0.305	10.21	0.980	0.052±0.02
$v_2 = 0.30$	2.55	0.358	11.14	0.898	0.125±0.02
$v_2 = 0.40$	2.36	0.419	12.76	0.784	0.224±0.03

Table 6. The Second Virial Coefficient and the Radius of Gyration for PIB in Solvent Mixtures

λ,Å	Temp. °C	Sol. Mixture	v_2	$A_2 \times 10^4$, ml./g.^{2}	R_G,Å
4358	35	Cyclohexane (1) Acetone (2)	0.00	4.55	645
4358	35	Cyclohexane (1) Acetone (2)	0.10	4.22	637
4358	35	Cyclohexane (1) Acetone (2)	0.15	3.11	614
4358	35	Cyclohexane (1) Acetone (2)	0.20	3.09	574
4358	35	Cyclohexane (1) Acetone (2)	0.25	2.53	535
4358	35	Cyclohexane (1) Acetone (2)	0.30	1.64	500
4358	25	Cyclohexane (1) Benzene (2)	0.20	4.55	650
5461	35	Cyclohexane (1) Acetone (2)	0.00	2.13	633
5461	35	Cyclohexane (1) Acetone (2)	0.10	1.93	624
5461	35	Cyclohexane (1) Acetone (2)	0.15	1.67	588
5461	35	Cyclohexane (1) Acetone (2)	0.20	1.63	570
5461	35	Cyclohexane (1) Acetone (2)	0.25	1.59	551
5461	35	Cyclohexane (1) Acetone (2)	0.30	0.62	492
5461	25	Cyclohexane (1) Benzene (2)	0.20	2.12	641

Table 7. The Second Virial Coefficient and the Radius of Gyration for PMMA in Solvent Mixtures at 25°C and 4358 Å

Tacticity of Polymer	Sol. Mixture	v_2	$A_2 \times 10^4$ ml./g.^{2}	R_G, Å
Syndiotactic	Acetone (1) Cyclohexane (2)	0.00	1.50	336
Syndiotactic	Acetone (1) Cyclohexane (2)	0.10	1.38	334
Syndiotactic	Acetone (1) Cyclohexane (2)	0.20	0.97	351
Syndiotactic	Acetone (1) Cyclohexane (2)	0.30	1.24	327
Syndiotactic	Acetone (1) Cyclohexane (2)	0.40	1.15	289
Atactic	Acetone (1) Cyclohexane (2)	0.00	---	116
Atactic	Acetone (1) Cyclohexane (2)	0.10	---	110
Atactic	Acetone (1) Cyclohexane (2)	0.20	---	101
Atactic	Acetone (1) Cyclohexane (2)	0.30	---	093
Atactic	Acetone (1) Cyclohexane (2)	0.40	---	085

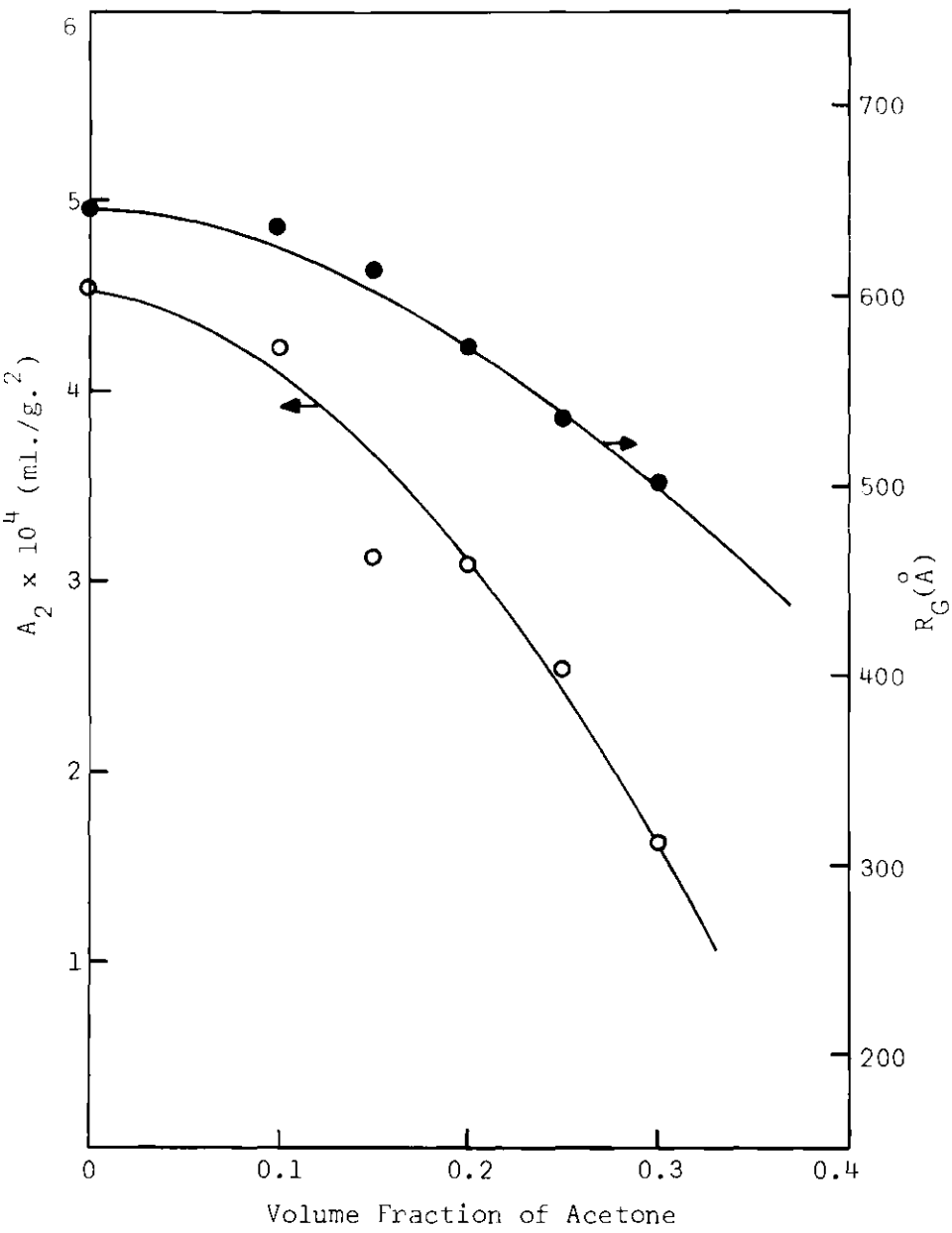


Figure 15. Second Virial Coefficient and Raius of Gyration as a Function of Mixed Solvent Composition for the System PIB-Cyclohexane-Acetone at 35°C and 4358 Å

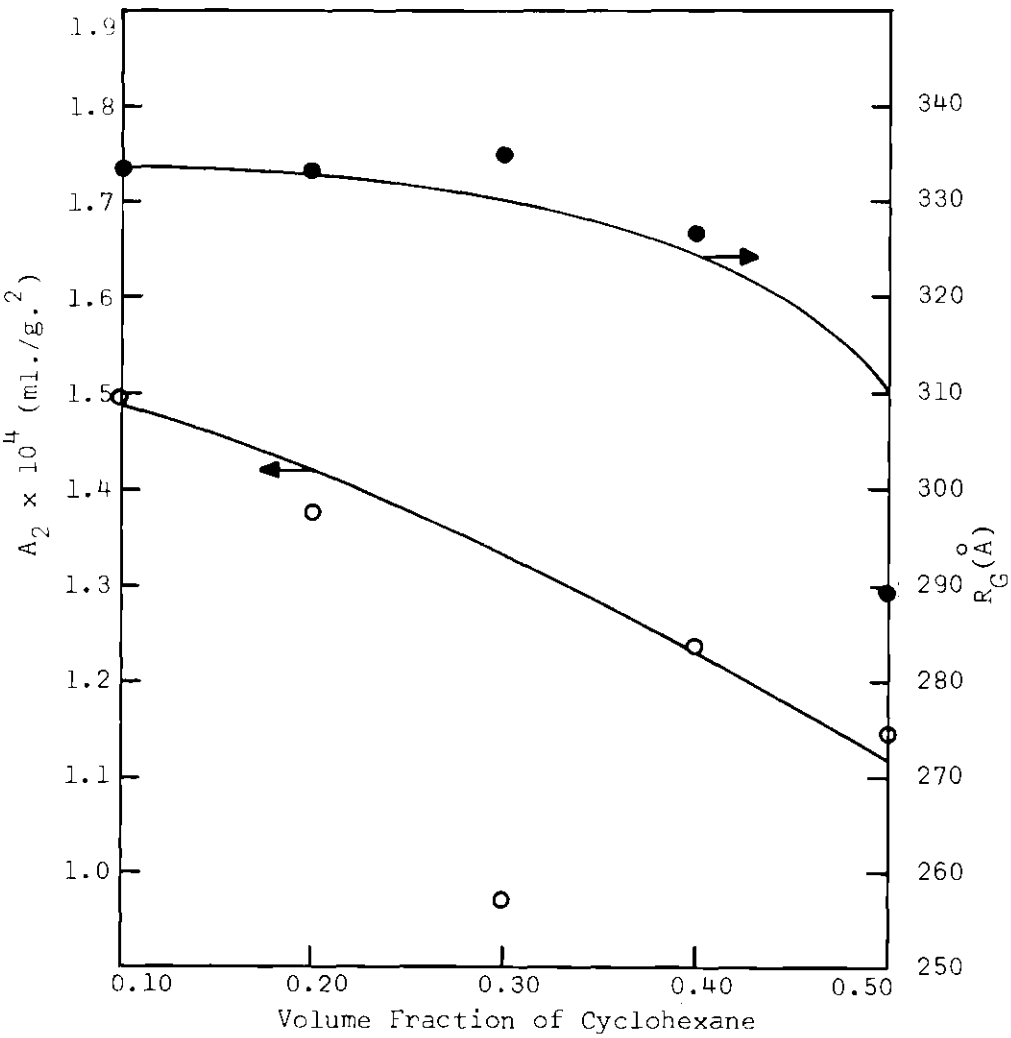


Figure 16. Second Virial Coefficient and Radius of Gyration as a Function of the Mixed Solvent Composition for the System Syndiotactic PMMA-Acetone-Cyclohexane at 25°C and 4358 Å

Second Virial Coefficient

The second virial coefficient A_2 is zero at the theta condition, where the excess chemical potential due to segment-solvent interaction is zero and deviations from ideality vanish. Polymer solutions show large deviations from this condition in good solvents due to the excluded volume effect. In good solvents the swelling of the polymer molecules is enhanced by the presence of the better solvent molecules in the vicinity of polymer segments. This increase in the excluded volume is responsible for the polymer solution deviating from theta conditions and leads to an increase in the second virial coefficient. In a poorer solvent medium there is a decrease in the excluded volume, which leads to a smaller value of A_2. Thus, the second virial coefficient is a measure of the solvent power of the medium. The poorer the solvent medium, the smaller the second virial coefficient. The experimental results are consistent with theoretical prediction. The values of A_2 decrease as the composition of the second (the poorer) solvent increases.

Radius of Gyration

The radius of gyration is a measure of the dimension of a random coil in the solution. For all the systems examined, the radius of gyration decreases with increasing the composition of non-solvent. This is in line with the trend of the values of the second virial coefficient discussed above. In a good solvent, the polymer molecules spread out and have large values of radius of gyration. In a poorer solvent the radius of gyration decreases because of the contraction of the swollen molecules.

Selective Adsorption

The System Cyclohexane (1)-Acetone (2)-PIB (3)

Figure 12 shows plots of kc/R_o versus c for this system at 4358 Å. When the composition of non-solvent increases, the slope decreases because of the shrinkage of the swollen polymer molecules. This occurs because of the increased preference for segment-segment contacts as the proportion of non-solvent increases. The change in intercept indicates the occurrence of selective adsorption. The theory of Ewart, et al., predicts that if the change in intercept is negative, the solvent component having the higher value of refractive index will be selectively adsorbed. Cyclohexane has a value of refractive index of 1.4200, which is higher than 1.3535 of acetone. Therefore, since the intercepts in Figure 12 are seen to decrease with increasing acetone concentration, cyclohexane is adsorbed. Recall Equation (15)

$$\alpha = \left[\left(\frac{\bar{M}_w^*}{\bar{M}_w}\right)^{\frac{1}{2}} - 1\right] \left(\frac{dn/dc}{dn/dv_1}\right) \qquad (15)$$

where $\bar{M}_w^*$ is the apparent weight average molecular weight. Values of $(dn/dc)_T$ and $(dn/dv_1)_T$ required for the calculation of α are listed in Appendix 18. The values of α calculated from Equation (15) for five different compositions of mixed solvent are shown in Table 1. Recall that the selective adsorbption constant α is a measure of the change in composition of the solvent mixture in vicinity of the polymer segments (Equation (11)). A positive value of α means that the volume fraction of cyclohexane outside the domain occupied by polymer

segments decreases; in other words, cyclohexane is adsorbed. Our experimental results are those which were expected in view of the fact that cyclohexane is a good solvent for PIB and would be expected to be adsorbed by the polymer molecules, whereas acetone is a non-solvent.

To compare these experimental results with theoretical predictions, we use Read's expression (Equation (17)) containing binary interaction parameters χ_{ij}.

$$\alpha = \bar{v}_3 v_1 v_2 \frac{\chi_2 \ell^{-1}(v_2 - v_1) + \chi_{23} - \chi_{13}\ell^{-1} + (\ell^{-1} - 1)}{v_1 + \ell^{-1} v_2 - 2(\chi_{12}\ell^{-1}v_1 v_2)} \qquad (17)$$

This equation is based on the Flory-Huggins expression for the chemical potential and accordingly possesses the same limitations as the Flory-Huggins theory. However, no vapor pressure-composition data for cyclohexane-acetone were available to calculate a value of χ_{12}. Hence χ_{12} was estimated by utilizing Hildebrand's "solubility parameter" theory: $\chi_{12} = (V_1/RT)(\delta_1 - \delta_2)^2$. Taking the value V_1 = 109.9 cc./mole, δ_1 = 8.20 and δ_2 = 9.9 (34), it is found that χ_{12} = 0.519 at 35°C. The parameter χ_{13} has been found to be 0.428 at 35°C (35). The parameter χ_{23} can not be found by direct measurement on the binary system since acetone is a non-solvent for PIB. Accordingly the experimental data for α and the value of χ_{12} and χ_{13} can be utilized in Equation (17) to calculate a value of χ_{23}. Such an indirect procedure is necessary to obtain an estimate for this parameter. For χ_{12} = 0.519, χ_{13} = 0.428 and several reasonable choices of χ_{23}, the values of α were calculated as a function of v_2 up to 0.40. These values are listed in Table 8 and are

plotted in Figure 17 along with the experimental values of α. From these calculations, the interaction parameter χ_{23} appears to be about 2.0 ± 0.1. This large value of PIB-acetone interaction signifies that acetone is a non-solvent for PIB. Although not precise, this method of assigning a value of χ_{23} is valuable, for there is no way to measure the interaction parameter between polymer and non-solvent directly.

Table 8. Theoretical Prediction of Adsorption Constant for PIB-Cyclohexane-Acetone System at χ_{12} = 0.519 and χ_{13} = 0.428

Vol. Fraction of Acetone	ADSORPTION CONSTANT α			
	χ_{23} = 1.50	χ_{23} = 2.00	χ_{23} = 2.50	χ_{23} = 3.00
0.00	0.000	0.000	0.000	0.000
0.05	0.031	0.059	0.086	0.113
0.10	0.066	0.121	0.175	0.230
0.15	0.104	0.185	0.266	0.347
0.20	0.144	0.251	0.357	0.464
0.25	0.186	0.316	0.447	0.577
0.30	0.228	0.380	0.532	0.684
0.35	0.269	0.440	0.611	0.782
0.40	0.306	0.493	0.680	0.867

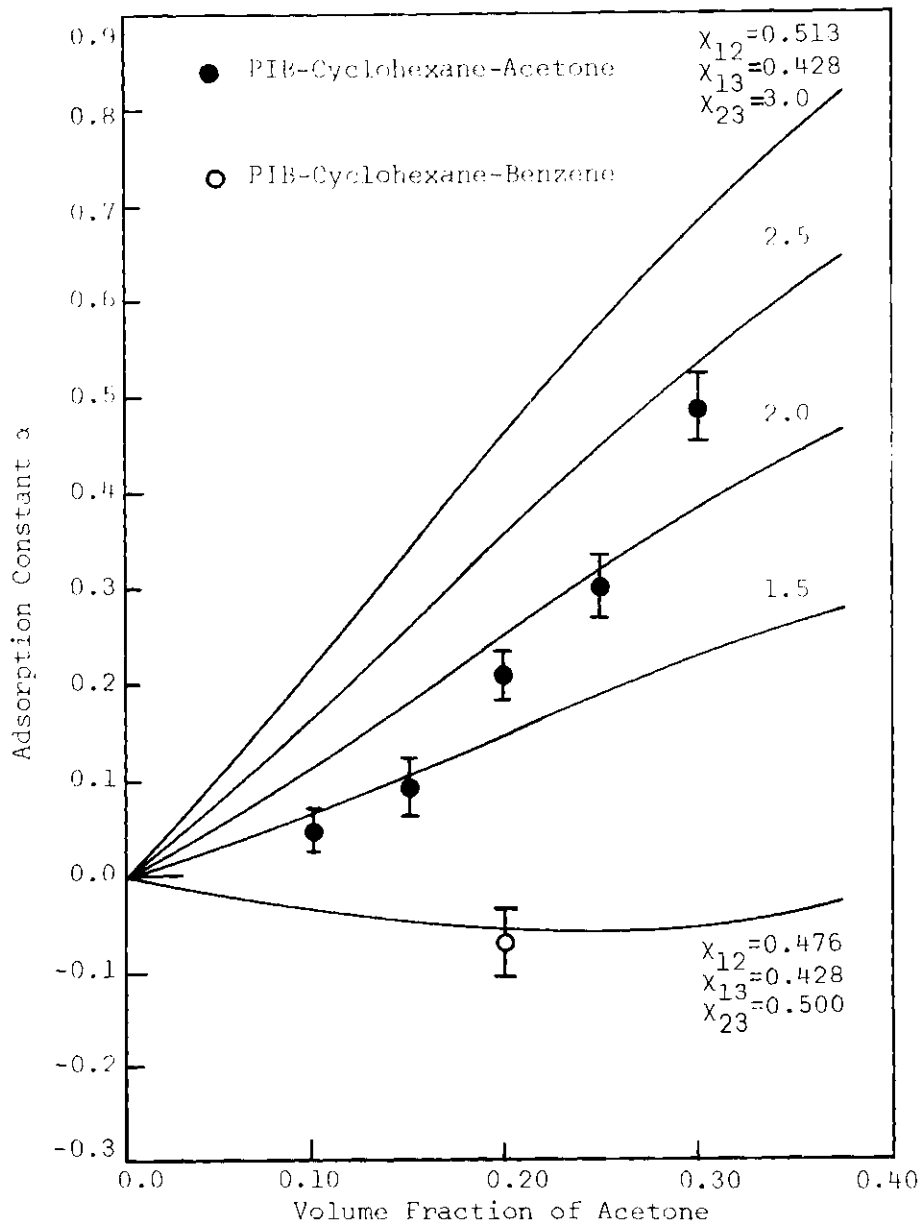


Figure 17. Comparison of Experimental and Theoretical Dependence of Adsorption Constant on the Composition of the Mixed Solvent for PIB L-80F

Figure 17 shows that the theoretical calculations do not fit our experimental results too well. This deviation could conceivably be due to the uncertainty in the values of χ_{12} and χ_{13}. However, adjusting these values of χ_{ij} failed to give a better fit to the experimental points. Therefore it is concluded that the theoretical description of selective adsorption constant given by Equation (17) is not adequate for this system. The same situation was also found by Read (14) and Cowie (15) from their studies of the systems benzene-cyclohexane-polystyrene and benzene-heptane-polystyrene, respectively. Read derived a more complex function by introducing a "three-body" interaction parameter χ_{123}. This more complex description of the adsorption constant allowed a better fit to their experimental results. Although this procedure seems sound enough, it was not followed in this work because of the difficulty in assigning a value to χ_{123} which is not completely arbitrary.

Both the experimental results and the calculations based on Equation (17) show that selective adsorption increases initially as the composition of non-solvent increases. At higher composition of non-solvent, α is predicted by Equation (17) to go through a maximum and then to decrease. The reason for this is that there is a preference for polymer segment-segment contacts in a very poor solvent, thus leaving fewer available sites for the adsorption of cyclohexane. The maximum in the adsorption constant was not observed experimentally in this work because of the difficulties encountered in filtering the solutions at high concentrations of acetone.

Each measurement was also made at λ = 5461 $\mathring{A}$ for this system.

The results of the selective adsorption are listed in Table 2. The molecular weights obtained are not equal to those of the measurements made at λ = 4358 Å. This difference could be due to the errors in the Rayleigh ratio of benzene. However, this constant error was canceled in the calculations of α from Equation (15). Comparison of the values of α shows that the results from two different wavelengths measurements are in good agreement within the experimental errors.

The System Cyclohexane (1)-Benzene (2)-PIB (3)

The measurement of light scattering of PIB (3) in the mixed solvent system of cyclohexane (1) and benzene (2) was less successful. The reason for this is that the refractive index of benzene (1.5149) is too close to that of PIB (1.5282). Consequently as the benzene concentration increases, the value of $(dn/dc)_T$ becomes too small for the measurement of the excess scattering to have sufficient precision to be reliable. Therefore only one successful measurement was performed: the scattering in 20 per cent by volume of benzene at 25°C. The values of $(dn/dc)_T$ and $(dn/dv_1)_T$ needed for the calculation of α are shown in Table 10. The Zimm plot for the data is shown in Figure 11. The value of the apparent weight average molecular weight $\bar{M}_w^*$ corresponding to the data obtained was 1.18×10^6. The corresponding value of α calculated from Equation (15) is -0.068 ± 0.01. This negative value of α means that benzene is preferentially adsorbed for this system. This result originally seemed surprising, since benzene is a poorer solvent for PIB than cyclohexane. It is possible that this experimental result is fortuitous because of the difficulties involved in obtaining good data for this system. However, taking χ_{12} = 0.476

(36), χ_{23} = 0.500 and χ_{13} = 0.428, theoretical values of α were calculated from Equation (17). This theoretical value of α, -0.055, is in good agreement with our experimental result. The theoretical curve is compared with the single experimental point in Figure 17.

Measurements at λ = 5461 Å on the same system give a result of α = -0.062 ± 0.01, again showing that benzene is selectively adsorbed.

Blaker and Badger (9) also reported a series of selective adorption measurement in which the poorer solvent was preferentially adsorbed. They assumed that there was a strongly attractive interaction between solvent molecules and the localized sites on the nonpolar faces of the polymer.

The System Acetone (1)-Cyclohexane (2)-PMMA (3)

Measurements on this system were made with unpolarized blue light (λ = 4358 Å) at a temperature of 25°C.

The results of light scattering measurements for syndiotactic and atactic PMMA are shown in Figure 12 and 13, respectively. The theory of Ewart, et al., predicts that if the change in intercept is positive, the solvent component having the lower value of refractive index will be selectively adsorbed. The refractive index of acetone (1.3652) is lower than that of cyclohexane (1.4329). Therefore acetone should be selectively adsorbed by the polymer segments. The experimental values of α calculated from Equation (15) for both syndiotactic and atactic PMMA are listed in Tables 4 and 5 and are shown in Figure 18. The values of $(dn/dc)_T$ and $(dn/dv_1)_T$ needed for the calculation of α are listed in Appendix 22. For each measurement acetone was preferentially adsorbed except for the measurement in 0.10 volume

fraction of cyclohexane, where cyclohexane was selectively adsorbed.

Taking $\chi_{12} = 0.361$ and $\chi_{13} = 0.479$ (35) and following the same treatment described above on the PIB-cyclohexane-acetone system, we found that χ_{23} appeared to be about 1.5 ± 0.1. The theoretical predictions of α are listed in Table 9 and are shown in Figure 18 together with the experimental results for comparison. Again Read's theoretical predictions do not fit our experimental results.

Table 9. Theoretical Prediction of Adsorption Constant for PMMA-Acetone-Cyclohexane System at $\chi_{12} = 0.361$ and $\chi_{13} = 0.479$

Vol. Fraction of Cyclohexane	ADSORPTION CONSTANT			
	$\chi_{23} = 1.0$	$\chi_{23} = 1.5$	$\chi_{23} = 2.0$	$\chi_{23} = 2.5$
0.00	0.000	0.000	0.000	0.000
0.05	0.012	0.033	0.053	0.074
0.10	0.027	0.067	0.108	0.148
0.15	0.046	0.103	0.161	0.219
0.20	0.066	0.139	0.212	0.286
0.25	0.087	0.173	0.260	0.346
0.30	0.107	0.204	0.301	0.398
0.35	0.127	0.231	0.336	0.440
0.40	0.144	0.253	0.362	0.471

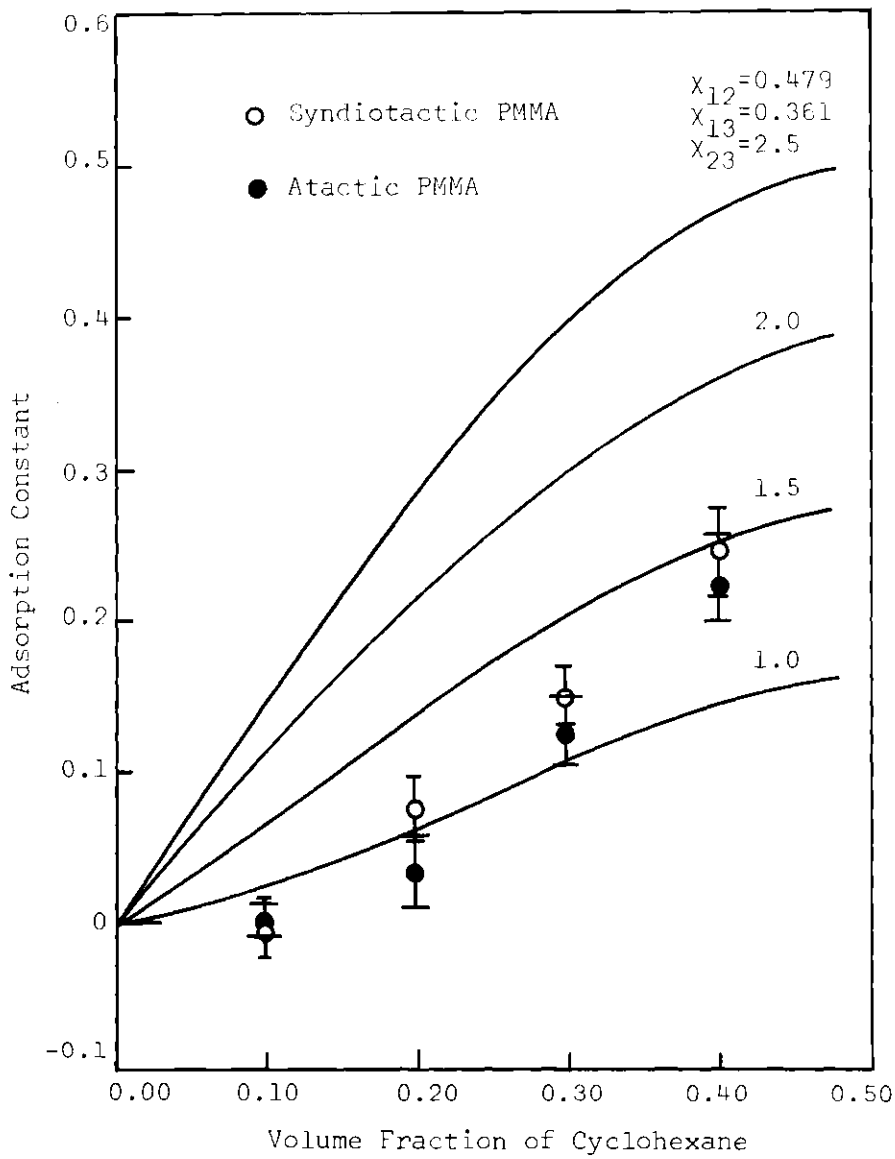


Figure 18. Comparison of Experimental and Theoretical Dependence of Adsorption Constant on Composition of the Mixed Solvent for Syndiotactic and Atactic PMMA

Comparing the difference in selective adsorption constants α for the atactic and syndiotactic PMMA, we conclude that, within the experimental errors (± 0.03), there is no influence on the selective adsorption by the local order of the side chain.

In Read's expression of the theoretical predictions, the important term that affects the selective adsorption is the numerator:

$$Q = \chi_{12}\ell^{-1}(v_2 - v_1) + (\chi_{23} - \chi_{13}\ell^{-1}) + (\ell^{-1} - 1)$$

Considering the case where V_1 and V_2 are nearly equal, we can rewrite the above equation as:

$$Q = \chi_{12}(v_2 - v_1) + (\chi_{23} - \chi_{13})$$

If the value of $(\chi_{23} - \chi_{13})$ is small and the solvent-solvent interaction is unfavorable, i.e., if $\chi_{12} > 0$, then the volume fraction of the component 2 is the adsorption-determining factor. At small value of v_2, $|\chi_{12}(v_2 - v_1)| > (\chi_{23} - \chi_{13})$. Then $Q < 0$ or $\alpha < 0$. Hence the component 2 is selectively adsorbed. For this system studied, the fact that cyclohexane was adsorbed at 0.10 volume fraction of cyclohexane indicates unfavorable molecular contacts between acetone and cyclohexane.

Although Read's theoretical description of selective adsorption is not applicable to the systems investigated, it is still useful for predicting which of the solvents will be adsorbed and to what extent, if the interaction parameters χ_{ij} are known.

CHAPTER IV

CONCLUSIONS

1. Light scattering measurements on the system polyisobutylene-cyclohexane (a good solvent)-acetone (a non-solvent) lead to the conclusion that the good solvent is preferentially adsorbed by the polymer molecules. By fitting the data to a Flory-Huggins type of equation, it is found that the interaction parameter χ_{23} between polyisobutylene segments and acetone molecules appears to be 2.0 ± 0.1, indicating that acetone is a non-solvent for polyisobutylene.

2. Similar measurements of the system polyisobutylene-cyclohexane (a good solvent)-benzene (a poor solvent) show that benzene is selectively adsorbed at a benzene concentration of 20 per cent by volume. The reason for this is that molecular contact between molecules of cyclohexane and benzene is unfavorable, as manifested in the rather large value of the parameter $\chi_{12} = 0.476$.

3. For the systems containing syndiotactic or atactic polymethylmethacrylate in a mixture of acetone (a good solvent) and cyclohexane (a non-solvent), acetone is selectively adsorbed except for the measurement in 0.10 volume fraction of cyclohexane, where cyclohexane is selectively adsorbed.

4. Within experimental error, the selective adsorption is not affected by the stereoregularity of the polymethylmethacrylate samples.

5. The second virial coefficients obtained in the mixed solvent systems exhibit the expected trend, decreasing with increasing amounts of the poorer solvent.

6. The radii of gyration obtained in the mixed solvent systems also exhibit the expected trend, decreasing with increasing amounts of the poorer solvent.

APPENDIX

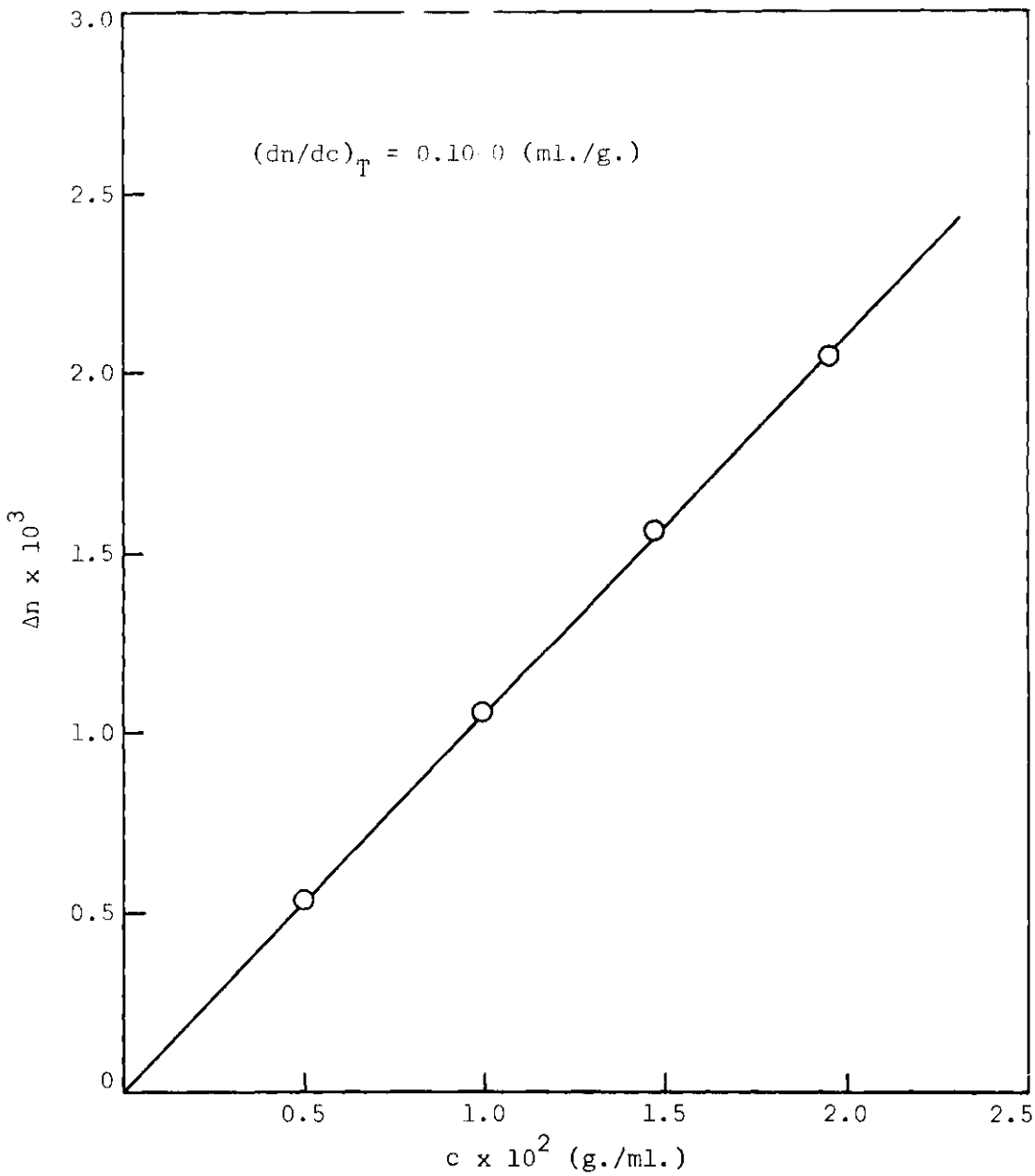
APPENDIX 1

MEASUREMENT OF $(dn/dc)_T$ FOR PIB IN PURE CYCLOHEXANE AT 35°C AND 4358 Å ($K_{4358} = 9.93 \times 10^{-4}$)

Solution	Solvent	SOLUTION 1	2	3	4
Conc. $\times 10^2$ g./ml.	0.000	0.4936	0.9871	1.4711	1.9521
d_1	4.892	5.166	5.418	5.671	5.911
d_2	4.909	4.644	4.387	4.122	3.874
$d_1 - d_2$	-0.017	0.522	1.031	1.549	2.037
Δd_T	0.000	0.539	1.048	1.566	2.054
$\Delta n \times 10^4$	---	5.3534	10.409	15.554	20.401
dn/dc, ml./g.	---	0.1084	0.1055	0.1057	0.1045

APPENDIX 2

DETERMINATION OF $(dn/dc)_T$ FOR PIB AT 4358 Å FROM APPENDIX 1



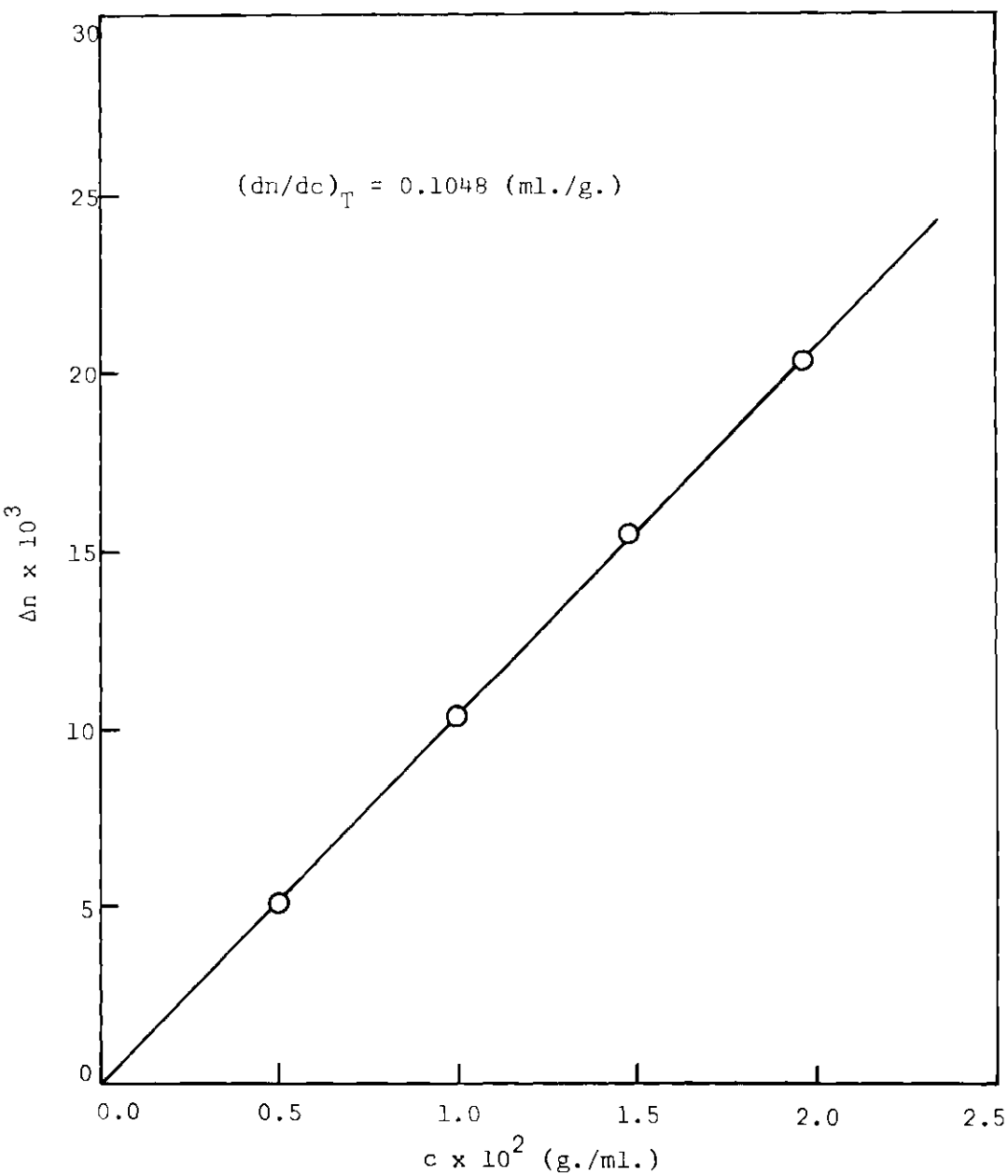
APPENDIX 3

MEASUREMENT OF $(dn/dc)_T$ FOR PIB IN PURE CYCLOHEXANE AT 35°C AND 5461 Å ($K_{5461} = 9.92 \times 10^{-4}$)

Solution	Solvent	SOLUTION 1	2	3	4
Conc. x 10^2 g./ml.	0.000	0.4936	0.9871	1.4711	1.9521
d_1	4.887	5.154	5.418	5.668	5.917
d_2	4.907	4.650	4.395	4.135	3.888
$d_1 - d_2$	-0.020	0.540	1.023	1.533	2.029
Δd_T	0.000	0.524	1.043	1.553	2.049
$\Delta n \times 10^4$	---	5.198	10.345	15.404	20.324
dn/dc, ml./g.	---	0.1053	0.1049	0.1047	0.1041

APPENDIX 4

DETERMINATION OF $(dn/dc)_T$ FOR PIB AT 5461 Å FROM APPENDIX 3



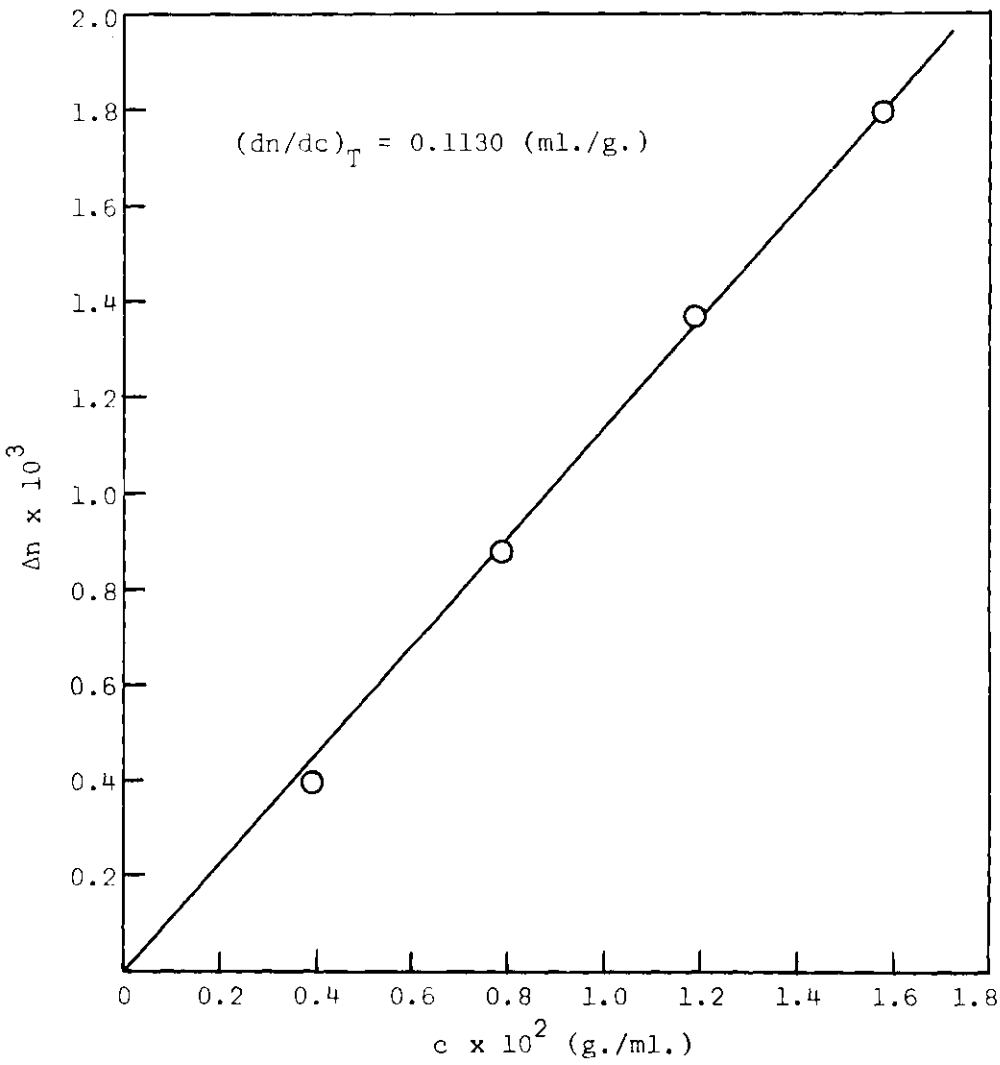
APPENDIX 5

MEASUREMENT OF $(dn/dc)_T$ FOR PIB IN 10 PER CENT OF ACETONE AT 35°C AND 4358 Å ($K_{4358} = 9.93 \times 10^{-4}$)

Solution	Solvent	SOLUTION 1	2	3	4
Conc. $\times 10^2$ g./ml.	0.000	0.3985	0.7856	1.1871	1.5740
d_1	4.941	5.137	5.383	5.621	5.893
d_2	4.963	4.768	4.520	4.267	4.106
$d_1 - d_2$	-0.022	0.369	0.863	1.354	1.781
Δd_T	0.000	0.391	0.885	1.376	1.803
$\Delta n \times 10^4$	---	3.884	8.790	13.670	17.910
dn/dc, ml./g.	---	0.0975	0.1119	0.1151	0.1138

APPENDIX 6

DETERMINATION OF $(dn/dc)_T$ FOR PIB IN 10 PER CENT ACETONE AT 4358 Å FROM APPENDIX 5



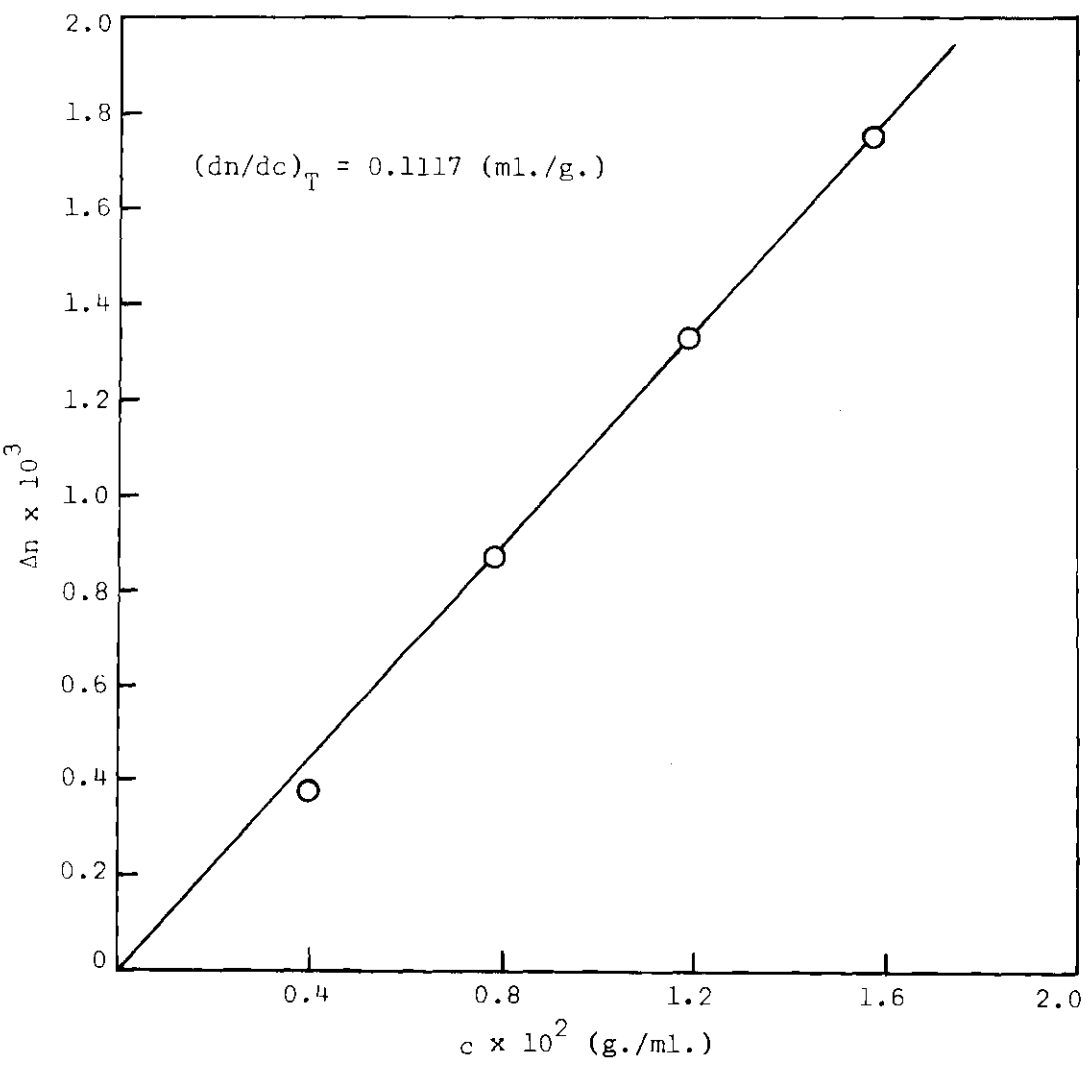
APPENDIX 7

MEASUREMENT OF $(dn/dc)_T$ FOR PIB IN 10 PER CENT OF ACETONE AT 35°C and 5461 Å ($K_{5461} = 9.92 \times 10^{-4}$)

Solution	Solvent	SOLUTION 1	2	3	4
Conc. x 10^2 g./ml.	0.000	0.3985	0.7856	1.1871	1.5740
d_1	4.939	5.127	5.380	5.622	5.892
d_2	4.964	4.771	4.522	4.309	4.148
$d_1 - d_2$	-0.025	0.356	0.858	1.313	1.744
Δd_T	0.000	0.381	0.883	1.338	1.769
$\Delta n \times 10^4$	---	3.779	8.758	13.271	17.550
dn/dc, ml./g.	---	0.095	0.112	0.112	0.112

APPENDIX 8

DETERMINATION OF $(dn/dc)_T$ FOR PIB IN 10 PER CENT ACETONE AT 5461 Å FROM APPENDIX 7



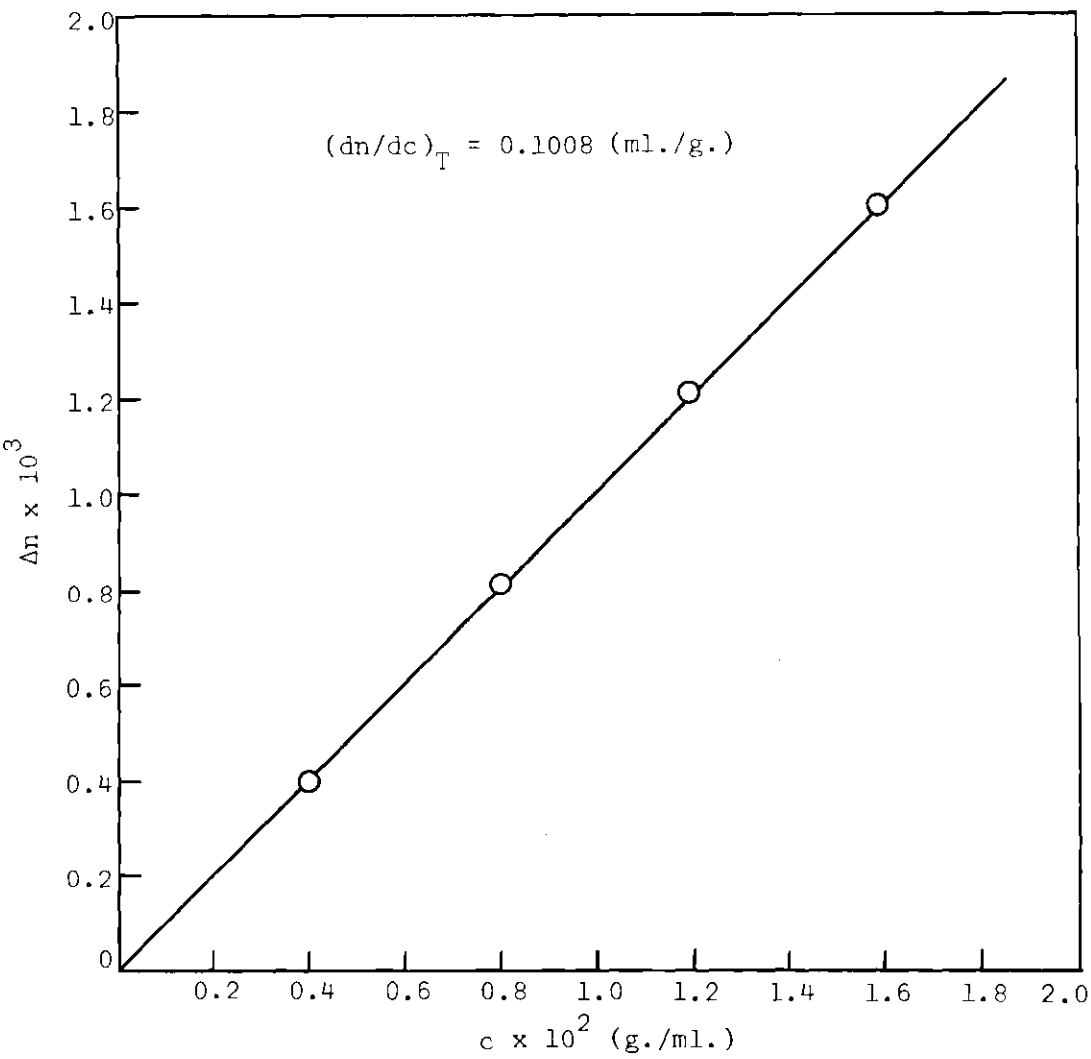
APPENDIX 9

MEASUREMENT OF $(dn/dc)_T$ FOR PIB IN PURE CYCLOHEXANE AT 25°C AND 4358 Å ($K_{4358} = 9.93 \times 10^{-4}$)

Solution	Solvent	SOLUTION 1	2	3	4
Conc. x 10^2 g./ml.	0.000	0.4036	0.8005	1.1950	1.5852
d_1	4.907	5.110	5.314	5.510	5.703
d_2	4.915	4.713	4.507	4.298	4.101
$d_1 - d_2$	-0.007	0.397	0.807	1.212	1.602
Δd_T	0.000	0.404	0.814	1.219	1.609
$\Delta n \times 10^4$	---	4.013	8.085	12.107	15.981
dn/dc, ml./g.	---	0.0994	0.1010	0.1013	0.1008

APPENDIX 10

DETERMINATION OF $(dn/dc)_T$ FOR PIB IN CYCLOHEXANE AT 25°C AND 4358 Å FROM APPENDIX 9



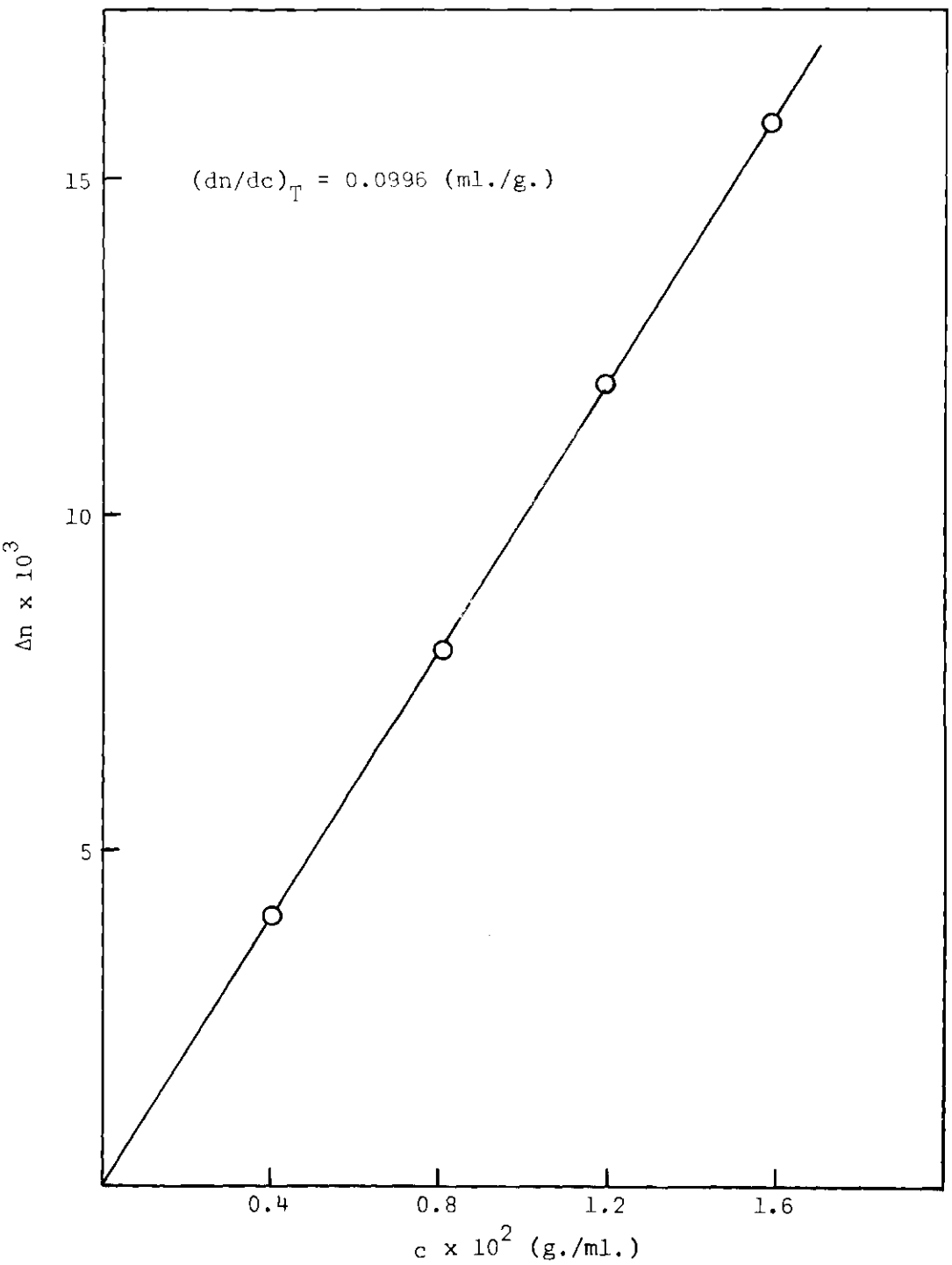
APPENDIX 11

MEASUREMENT OF $(dn/dc)_T$ FOR PIB IN PURE CYCLOHEXANE AT 25°C AND 5461 Å ($K_{5461} = 9.92 \times 10^{-4}$)

Solution	Solvent	SOLUTION 1	2	3	4
Conc. x 10^2 g./ml.	0.000	0.4036	0.8005	1.1950	1.5852
d_1	4.907	5.108	5.369	5.505	5.699
d_2	4.914	4.717	4.516	4.307	4.111
$d_1 - d_2$	-0.007	0.391	0.793	1.197	1.588
Δd_T	0.000	0.398	0.800	1.204	1.595
$\Delta n \times 10^4$	---	3.948	7.935	11.942	15.821
dn/dc, ml./g.	---	0.0978	0.0991	0.0994	0.0998

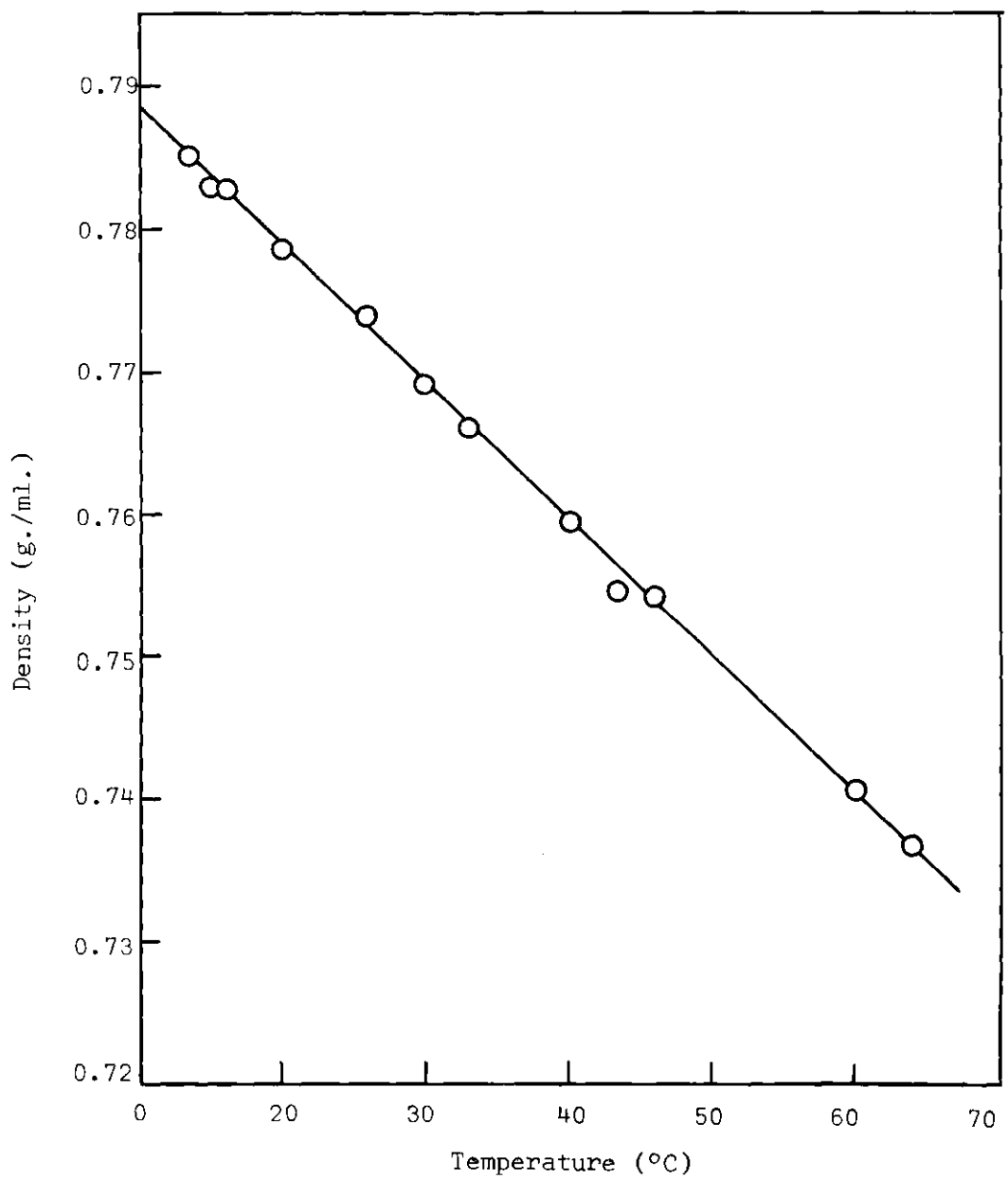
APPENDIX 12

DETERMINATION OF $(dn/dc)_T$ FOR PIB IN CYCLOHEXANE AT 25°C AND 5461 Å FROM APPENDIX 11



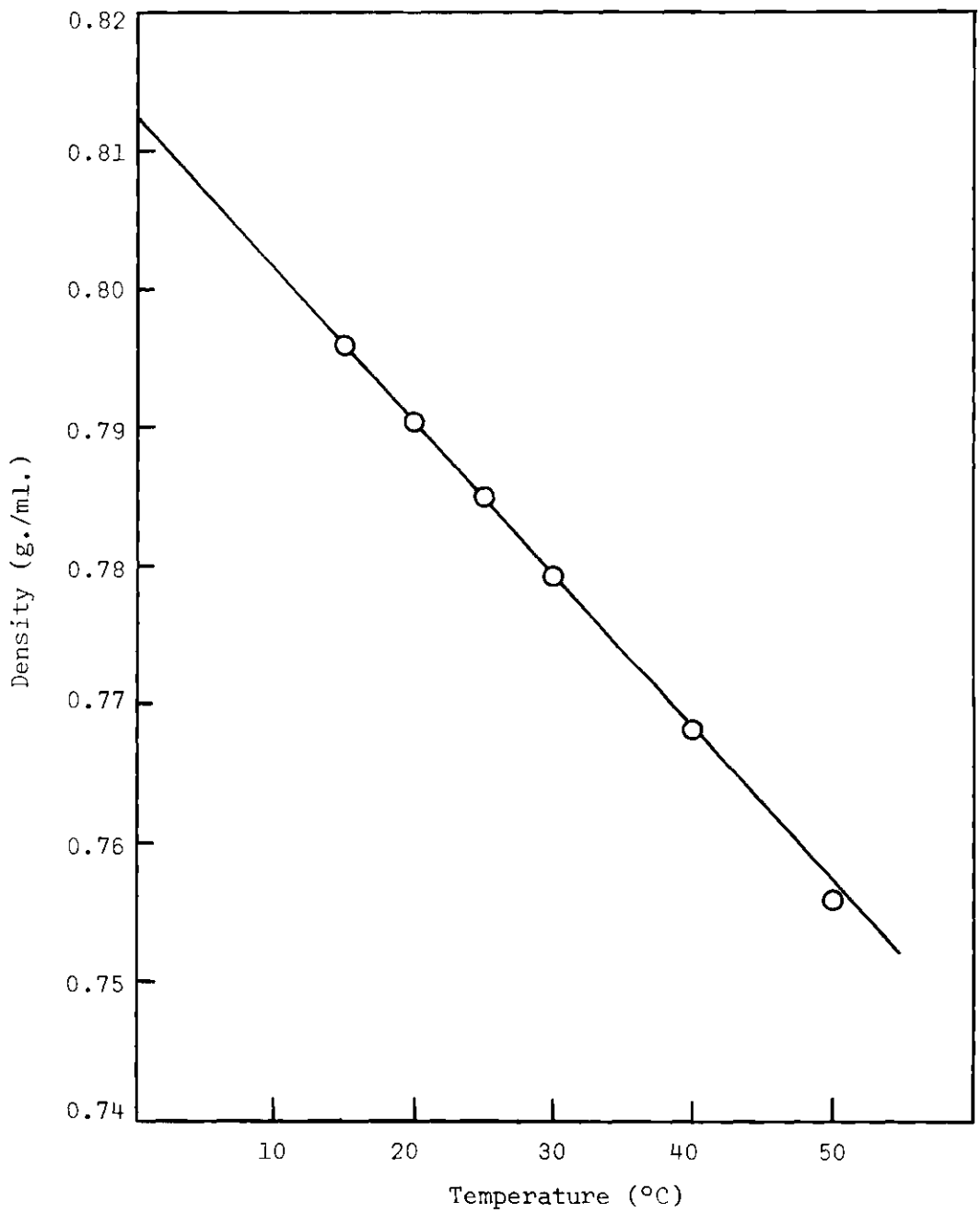
APPENDIX 13

DENSITY-TEMPERATURE CURVE ON CYCLOHEXANE



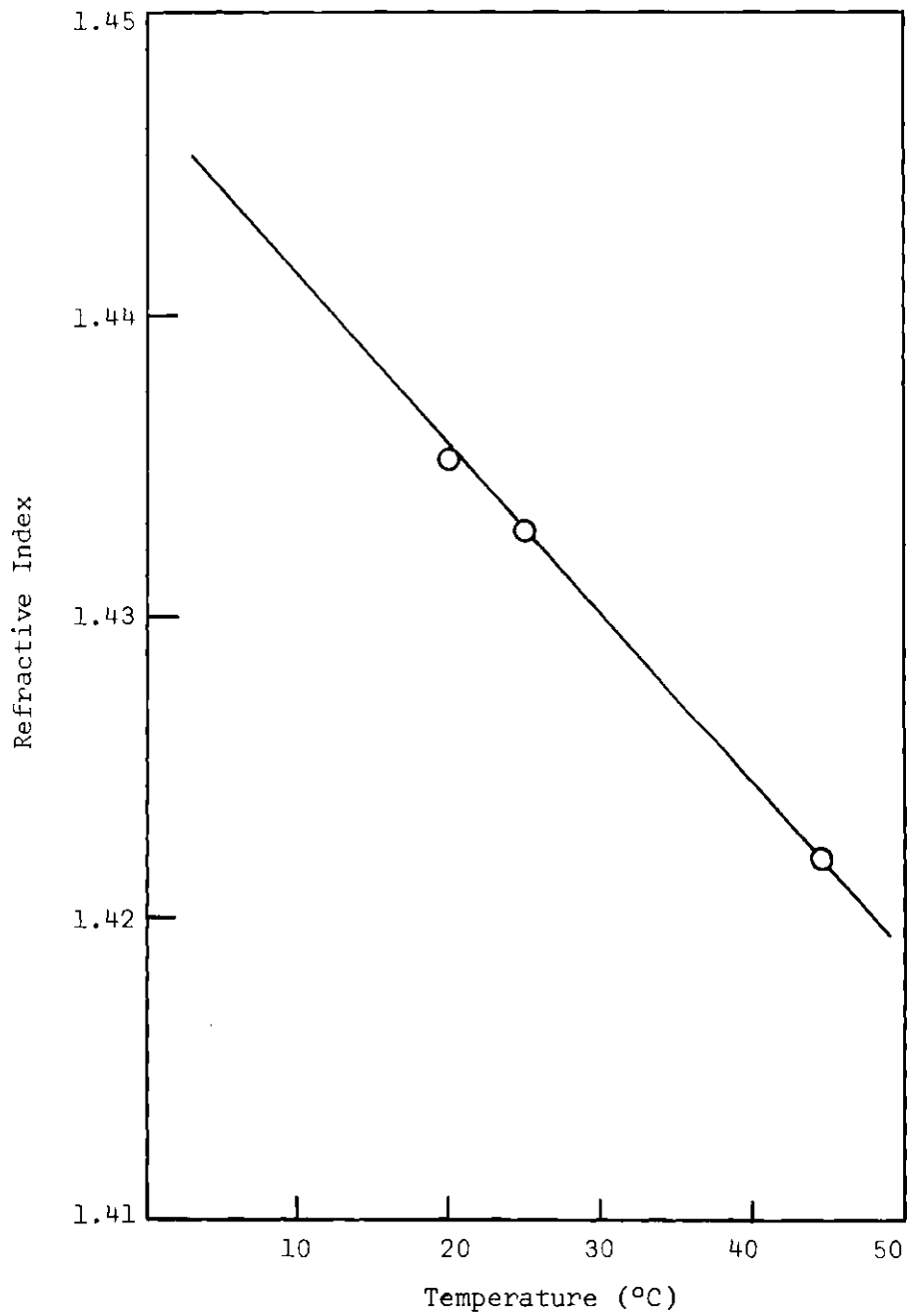
APPENDIX 14

DENSITY-TEMPERATURE CURVE ON ACETONE



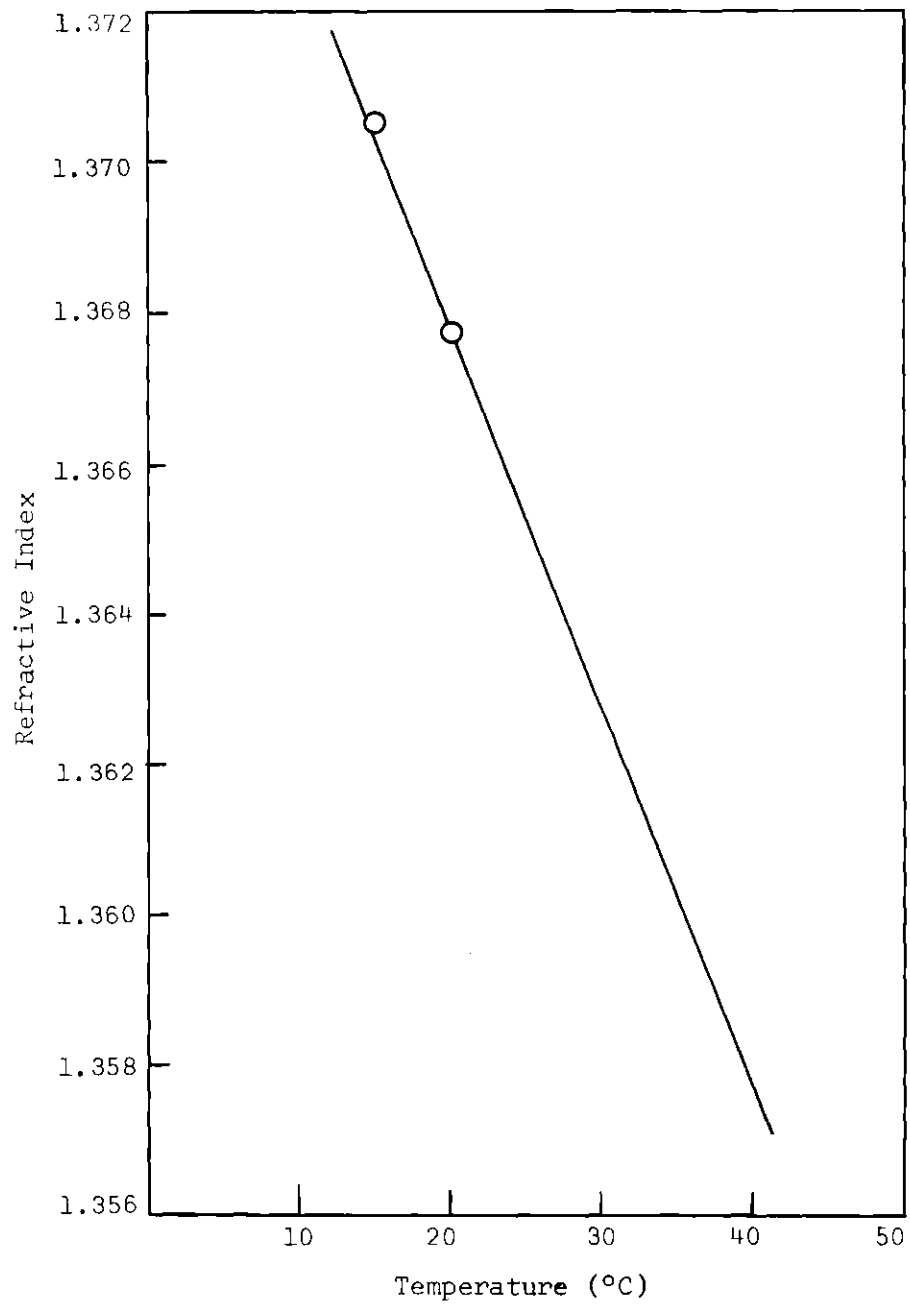
APPENDIX 15

REFRACTIVE INDEX OF CYCLOHEXANE AS A FUNCTION OF TEMPERATURE



APPENDIX 16

REFRACTIVE INDEX OF ACETONE AS A FUNCTION OF TEMPERATURE



APPENDIX 17

THE REFRACTIVE INDEX AND DENSITY OF POLYMER AND SOLVENT

Physical Constant	REFRACTIVE INDEX				Density, g./ml.	
	4358 Å		5461 Å			
Temperature	35°C	25°C	35°C	25°C	35°C	25°C
PIB	1.5277	1.5282	1.5191	1.5195	0.9130	0.9130
PMMA		1.5356				1.180
Cyclohexane	1.4273	1.4329	1.4200	1.4255	0.7643	0.7737
Acetone	1.3602	1.3652	1.3535		0.7738	0.7850
Benzene		1.5194		1.5020		0.8737

APPENDIX 18

CALCULATION OF $(dn/dv_1)_{c_3=0}$ AND $(dn/dc)_T$ FOR PIB IN MIXED SOLVENT OF CYCLOHEXANE AND ACETONE AT 35°C AND 4358 Å

Vol. Fraction of Acetone	Density d, g./ml.	Ref. Index n	$(dn/dc_2)_{c_3=0}$	$(dn/dv_1)_{c_3=0} = -d_2(dn/dc)_{c_3=0}$	$(dn/dc)_T$ ml./g.
v_2=.00	0.7643	1.4273	-0.08886	0.06876	0.1060
v_2=.05	0.7648	1.4239	-0.08865	0.06859	0.1095
v_2=.10	0.7652	1.4203	-0.08843	0.06842	0.1130
v_2=.15	0.7657	1.41701	-0.08822	0.06826	0.1165
v_2=.20	0.7662	1.4136	-0.08800	0.06809	0.1199
v_2=.25	0.7667	1.4102	-0.08779	0.06793	0.1233
v_2=.30	0.7671	1.4068	-0.08758	0.06777	0.1268
v_2=.35	0.7676	1.4034	-0.08738	0.06761	0.1302
v_2=.40	0.7681	1.4001	-0.08717	0.06745	0.1335

APPENDIX 19

CALCULATION OF $(dn/dv_1)_{c_3=0}$ AND $(dn/dc)_T$ FOR PIB IN MIXED SOLVENT OF CYCLOHEXANE AND ACETONE AT 35°C AND 5461 Å

Vol. Fraction of Acetone	Density d, g./ml.	Ref. Index n	$(dn/dc_2)_{c_3=0}$	$(dn/dv_1)_{c_3=0} = -d_2(dn/dc_2)_{c_3=0}$	$(dn/dc)_T$ ml./g.
$v_2=0.00$	0.7643	1.4200	-0.08800	0.0681	0.1048
$v_2=0.05$	0.7648	1.4166	-0.08779	0.06793	0.1082
$v_2=0.10$	0.7652	1.4132	-0.08758	0.06776	0.1117
$v_2=0.15$	0.7657	1.4098	-0.08737	0.06760	0.1151
$v_2=0.20$	0.7662	1.4064	-0.08716	0.06744	0.1182
$v_2=0.25$	0.7666	1.4031	-0.08696	0.06728	0.1219
$v_2=0.30$	0.7671	1.4000	-0.08675	0.06712	0.1253
$v_2=0.35$	0.7676	1.3964	-0.08655	0.06697	0.1287
$v_2=0.40$	0.7681	1.3930	-0.08635	0.06681	0.1321

APPENDIX 20

CALCULATION OF $(dn/dv_1)_{c_3=0}$ AND $(dn/dc)_T$ FOR PIB IN MIXED SOLVENT OF CYCLOHEXANE AND BENZENE AT 25°C AND 4358 Å

Vol. Fraction of Benzene	Density d, g./ml.	Ref. Index n	$(dn/dc_2)_{c_3=0}$	$(dn/dv_1)_{c_3=0} = -d_2(dn/dc_2)_{c_3=0}$	$(dn/dc)_T$ ml./g.
v_2=.00	0.7737	1.4329	0.09594	-0.08382	0.1008
v_2=.05	0.7787	1.4371	0.09623	-0.08407	0.0965
v_2=.10	0.7837	1.4413	0.09652	-0.08433	0.0922
v_2=.15	0.7887	1.4455	0.09682	-0.08459	0.0878
v_2=.20	0.7937	1.4498	0.09711	-0.08484	0.0834
v_2=.25	0.7987	1.4540	0.09741	-0.08511	0.0791
v_2=.30	0.8037	1.4583	0.09772	-0.08537	0.0746
v_2=.35	0.8087	1.4625	0.09802	-0.08564	0.0702
v_2=.40	0.8137	1.4668	0.09833	-0.08591	0.0657

APPENDIX 21

CALCULATION OF $(dn/dv_1)_{c_3=0}$ AND $(dn/dc)_T$ FOR PIB IN MIXED SOLVENT OF CYCLOHEXANE AND BENZENE AT 25°C AND 5461 Å

Vol. Fraction of Benzene	Density d, g./ml.	Ref. Index n	$(dn/dc_2)_{c_3=0}$	$(dn/dv_1) = -d_3(dn/dc_2)_{c_3=0}$	$(dn/dc)_T$ ml./g.
$v_2=0.00$	0.7737	1.4255	0.0852	-0.07444	0.09956
$v_2=0.05$	0.7787	1.4292	0.0854	-0.07464	0.09574
$v_2=0.10$	0.7837	1.4329	0.0857	-0.07484	0.09190
$v_2=0.15$	0.7887	1.4367	0.0859	-0.07504	0.08804
$v_2=0.20$	0.7937	1.4404	0.0861	-0.07524	0.08415
$v_2=0.25$	0.7987	1.4442	0.0864	-0.07545	0.08025
$v_2=0.30$	0.8037	1.4480	0.0866	-0.07565	0.07633
$v_2=0.35$	0.8087	1.4518	0.0868	-0.07586	0.07238
$v_2=0.40$	0.8137	1.4556	0.08707	-0.07607	0.06842

APPENDIX 22

CALCULATION OF $(dn/dv_1)_{c_3=0}$ AND $(dn/dc)_T$ FOR PMMA IN MIXED SOLVENT OF ACETONE AND CYCLOHEXANE AT 25°C AND 4358 Å

Vol. Fraction of Cyclohexane	Density d,g./ml.	Ref. Index n	$(dn/dc_2)_{c_3=0}$	$(dn/dv_1)_{c_3=0} = -d_2(dn/dc)_{c_3=0}$	$(dn/dc)_T$ ml./g.
v_2=.00	0.7850	1.3652	0.08551	-0.06616	0.1360
v_2=.05	0.7845	1.3685	0.08570	-0.06631	0.1335
v_2=.10	0.7839	1.3718	0.08589	-0.06646	0.1310
v_2=.15	0.7833	1.3751	0.08609	-0.06661	0.1285
v_2=.20	0.7828	1.3785	0.08629	-0.06676	0.1259
v_2=.25	0.7822	1.3818	0.08649	-0.06691	0.1234
v_2=.30	0.7816	1.3852	0.08669	-0.06707	0.1208
v_2=.35	0.7811	1.3885	0.08689	-0.06723	0.1183
v_2=.40	0.7805	1.3919	0.08709	-0.06738	0.1157

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BIOGRAPHY

The author was born on June 22, 1940 in Taiwan, China. He received his elementary education in his native town. He then attended Ping-Tung Senior High School, where he graduated in the summer of 1959. In the fall of that year he entered the Engineering College of Taiwan Provincial Cheng Kung University. Under the practical training program of his *alma mater*, he worked for the Taiwan Aluminum Corporation during the summer vacation of his Sophomore year. In 1963 he graduated with a degree of Bachelor of Science in Chemical Engineering. Shortly after his graduation from the college, he entered service in the Chinese Army as a Second Lieutenant, where he was assigned as a Unit Administration Officer. After his military service was completed, he enrolled at the Georgia Institute of Technology as a Graduate Teaching Assistant.

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